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THE
CHEMICAL NEWS

AND

JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

A Journal of Practical Chemistry

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

VOLUME CXVI.—1917.

145512
15/4/11

LONDON:
PUBLISHED AT THE OFFICE, 16, *NEWCASTLE STREET, FARRINGDON ST.*,
E.C. 4.
AND SOLD BY ALL BOOKSELLERS.

MDCCCCXVII.

THE CHEMICAL NEWS.
VOLUME CXVI.
EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.
No. 3006.—JULY 6, 1917.

THE VOLUMES OF THE ATOMS AT ABSOLUTE ZERO.

By GERVAISE LE BAS.

THE volumes of a large number of atoms in the combined condition throughout the liquid state have now been calculated. An attempt will now be made to ascertain the volumes of a number of them under similar conditions at absolute zero. Fortunately the requisite data are at hand, so that by a reasonable extrapolation it is possible to calculate the molecular volumes of a number of compounds at absolute zero and so the atomic volumes.

The following compounds have been studied at 17° C. and at −185° C., and from the densities under these conditions the requisite results have been obtained. (Table A).

By means of these results it can be shown that—(*a*) the volume of combined hydrogen is approximately 2·340, and (*b*) the relative volumes of the other atoms are :—

$$C = 4N, \quad N = 4H, \quad Cl = 6H, \quad O_2 = 5H, \quad >O = 3H.$$

A.

Substances (solids).	V_{-273}.	W.	V/W.
NH_4Cl	32·71	14	2·336
$(CO_2CH_3)_2$	74·80	32	2·337
$C_{10}H_8$	100 66	43	2·341
$(CO_2H)_2 2H_2O$ . ..	72·25	30	2·408
$CCl_3CH(OH)_2$	82 69	35	2·360
Average			2·356

$V(I_2)$	50·57	I	25·28	I = 10·8 H
$VCHI_3$ ..	86 00			
Less CH ..	11·70			
I_3	74·30	I	24·76	I = 10·6 H
		Average		10·7 H

At the critical point V_c = 100·3 or I = 10·4. The relative volumes are thus similar under the two conditions.

The volume of ammonium chloride, NH_4Cl, at the critical point may be calculated as follows :—

	V_a at critical point.
N	38·0 (*a*)
4H	38·6 (*b*)
Cl	57 9 (*b*)
ΣnV_a	134·5

$$\frac{V_c}{V_0} (NH_4Cl) = \frac{134·5}{32·71} = 4·11.$$

This ratio is a most important one. Similar values have been obtained by other observers, Heilborn, Guye, &c. It is not far from E. O. Meyer's value, $3\sqrt{2}$.

B.

Utilising this ratio it is now possible to calculate the volumes of *n*-pentane, hexane, at absolute zero, and so the volume of H under similar conditions.

Paraffin.	W.	V_c.	V_0.	V_0/V_w.
C_5H_{12}	32	309·3	75·2	2·350
C_6H_{14}	38	366·1	89 8	2·345

C.

The volume of H at absolute zero may also be calculated from the molecular volumes of the complex *n*-paraffin. At the melting-point (Krafft's data, *Ber.*, xv., 1687, 1711), assuming that there is no contraction on solidification in the normal paraffins, and that the contractions are proportional to the intervals of temperature before the melting-points. (Table B).

The whole series may be studied in a similar way, but these examples are sufficient. Thus ample confirmation of the atomic volume of hydrogen at absolute zero is obtained.

The volumes of the other atoms can be calculated under the circumstances by means of the integral relations already shown.

These ratios thus apply in the above instances throughout the solid and liquid states from absolute zero to the critical point. This result is important from a theoretical point of view (see *Science Progress*, 1914, xxxii., 663).

It may be noted that the relative volumes of oxygen in chloral hydrate and in hydrated oxalic acid are o = 3H. The formula in the latter case may thus be $C(OH)_3.C(OH)_3$.

Naphthalene, C_5H_8, manifests a contraction of 5 units, which it is necessary to attribute to the unsaturated linkages. It has also been shown by the writer (Monograph, p. 7) that the contraction for unsaturation in dodecylene, istradecylene, hexadecylene, and octodecylene is Δ = −2·56 in the liquid state at the melting-point.

It is thus fairly certain that the unsaturated linkages in the olefines, acetylenes, and in unsaturated ring compounds give rise to contractions. This subject is now receiving careful attention.

One point of extreme importance remains to be considered. If the volumes of the *n*-paraffins at absolute

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(*a*) See van't Hoff's "Text Book," *Phys. Chem.*, iii., 34.
(*b*) See Monograph, "The Moleculat Volumes of Liquid Compounds."

TABLE A.

Substances	d_{15}.	V_m.	d_{-185}	V_m.	Δ_V/Δ_T.	V_{-273} [by extra
NH_4Cl	1·5188	35·22	1·5757	33·96	0·0143	32·71
$(CO_2CH_3)_2$	1·4260	82 75	1·5278	77·24	0 0277	74·80
$(CO_2H)_2 2H_2O$ . .	1·6145	78·04	1·7024	74·01	0·0200	72·25
$CCl_3.CH(OH)_2$	1·9151	86·42	1·9744	83·82	0·0128	82·69
CHI_3	4·1955	93·56	4·4159	88·29	0·0260	86·6
$C_{10}H_8$	1·1589	110·45	1·2355	103·69	0 0344	100 66

TABLE B.

n-Paraffin.			M.W.	V_{-273}.	W.	V_0/W.
$C_{35}H_{72}$	$d_{74·7}$ 0·7816 $d_{99·2}$ 0·7664 d_{-273} 0·9973	Δ 0·00062	492	496·6	212	2·342
$C_{31}H_{64}$	$d_{68·1}$ 0 7808 $d_{98·8}$ 0·7619 d_{-273} 0·9767	Δ 0·000618	438	441·4	188	2·347
$C_{20}H_{42}$	$d_{36·7}$ 0·7779 $d_{99·2}$ 0·7363 d_{-273} 0·9840	Δ 0·000665	282·0	286 6	122	2·349

zero be compared with their molecular refractions, a most significant relation is obtained.

Substance.	V_0.	B_aM_a.
C_5H_{12}	75·2(3×25·07)	25·1
C_6H_{14}	89·1(3×29 7)	29·8

It is thus seen that the ratio—

$$V_0/M_a = 3·0, \text{ almost exactly.}$$

r_a (H) = 0·780 has already been pointed out by the writer, and V_a (H) = 2·34 = 3×0·780.

The volumes of the atoms at absolute zero are thus three times the volumes of the nuclei. The ratio of the volumes of the nuclei and the shells which surround them is as 1 : 2.

It is now possible to obtain some idea of the internal conditions of molecules. The atoms consist of nuclei surrounded by dielectric shells of twice the volume. The former are probably impermeable to light; the latter transmit the ethereal vibrations.

In unsaturated compounds there is an expansion of the nucleus. If it be supposed that this results in an additional attraction of contiguous nuclei owing to the inherent power of attraction of the nuclear substance of one atom for the nuclear substance of another atom across the dielectric shell, then it is necessary to suppose that this results in a compression of the dielectric shell itself. In this way all the facts observed may be explained. This condition results in a compact arrangement of the atoms.

The three most important relations which have been found to exist are:—

(a) V_{-273} (H) = 2·340.
(b) V_c/V_0 = 4·11.
(c) V_0/M_a = 3·0.

Special Reports on the Mineral Resources of Great Britain.—The Board of Agriculture and Fisheries desire to give notice of the publication of a second edition of Vol. IV. of the "Special Reports on the Mineral Resources of Great Britain," which have been prepared by the Director of the Geological Survey in response to numerous enquiries that have arisen through the conditions brought about by the war. In the main, it is a reprint of the first edition, wherein the properties, sources, and uses of fluorspar, and details of all workings in Britain, active and inactive, are given. Price 9d. Copies may be obtained through any bookseller, from Messrs. T. Fisher Unwin, Ltd., 1, Adelphi Terrace, London, W.C. 2 (who are the Sole Wholesale Agents to the Trade outside the County of London), or from the Director-General, Ordnance Survey Office, Southampton.

THE ADSORPTION OF CHROMIUM OXIDE BY HIDE POWDER.

By A. W. DAVISON

THE question as to the constitution of leather is still a widely debated one. The adherents of the chemical compound theory on the one hand are pitted against the supporters of the physical adsorption theory on the other. Neither faction is ready to accept, in their entirety, the claims of the other. As a representative of those supporting the chemical compound viewpoint, Fahrion (*Zeit. Angew. Chem.*, 1909, xxii., 2, 2083, 2135, 2187) points out that leather is a salt, in which the ex-dised hide, being amphoteric in character, may play the role of either acid radical or basic radical; and the tanning agent, that of basic or acid radical. Whether the hide functions as acid or base will depend solely upon the character of the tanning agent.

The adherents of the physical adsorption theory believe that the changes wrought in hides by tanning are of a physical rather than a chemical nature; and that they are analogous to those brought about in cotton by mercerisation; rubber by vulcanisation; or in cellulose by nitration; all of which are now regarded as adsorption phenomena.

Some authors go a step further, and claim that although the process of tanning is one of adsorption, pure and simple, further slow changes may take place with time. Stiasny (*Zeit. Kolloid. Chem.*, 1908, ii., 257) hold that since in the majority of cases tan stuffs are taken up from their colloidal solutions, the adsorption becomes immediately irreversible. He does not deny that slow chemical reactions may later take place between the hide fibre and the tanning agent.

As a preliminary to some extended work on the theory of tanning which is to be carried on in this laboratory, it was deemed desirable to substantiate, if possible, the claims of the physical theorists that the first process in tanning is one of straight adsorption. Further, and later changes, of whatever nature, are without the province of this paper.

The author has chosen the phase rule method of attack, because it so readily lends itself to the solution of problems of this character. Chromium has been selected as the tanning agent, since it, as a typical metallic tan, affords ease and certainty of analysis.

Although chromium salts are known to harden gelatine (Neuner, *Zeit. Kolloid. Chem.*, 1911, viii., 144) it was believed to be more advisable to use hide powder as the adsorbing agent, for the reason that one would thereby be working nearer to actual tanning conditions; and he could be more certain of dealing with a uniform, readily replaceable material. The hide powder used was the variety known as American Standard, obtained from Daigger and Company, Chicago. Although this product is somewhat coarse, it was found to be sufficiently porous to be thoroughly permeated by the tanning solutions. The powder was kept in a tightly closed metal can, and was weighed directly, without previous treatment, into the shaking flasks.

The tanning solution was made after a "single bath" formula by Flemming ("Practical Tanning," p. 225). Transposed into the metric system, this formula calls for: Solution A chrome alum, 120 grms. in 1000 cc. water; Solution B sodium carbonate, 30 grms. in 100 cc. water. Solutions A and B are to be slowly mixed, and any resulting precipitate removed by filtration. Throughout the remainder of this article the resulting solution is called "strong tan solution."

The final solution in which hides are to be tanned consists, for, say, ten kilogrms. of wet skin:—

Strong tan solution	2·5 litres
Water	66·3 litres
Salt	70·0 grms.

After the tanning process has been going on an hour, two and a half additional litres of strong tan solution should be added: this addition of strong tan solution should be continued until the hides are fully tanned. In all, about eight litres of strong tan solution are said to be required for ten kilogrms. of skin.

In order that conditions in all of the tanning flasks might be perfectly uniform, it seems desirable to complete the impregnation of the hide fibres at one operation. The usual method of "strengthening up" the solution after each hour leaves entirely too much uncertainty of equilibrium. Then, too, when one is dealing with powdered hide, which has previously been soaked in salt water, there is no tendency toward "case hardening," or uneven tanning, because the solution so easily permeates the entire fibrous mass. At least, in these experiments, microscopic examination of the tanned powder failed to reveal uneven tanning.

The soaking and tanning operations were carried out in 500 cc. rubber stoppered Erlenmeyer flasks. These were clamped to a rotating device in such a manner that the flasks were turned about a horizontal shaft perpendicular to their axis of symmetry. The radius of rotation was twelve inches; the flasks revolved fifty times per minute. This insured perfect agitation, since the total volume of solution in each 500 cc. flask was only 275 cc. The whole device was immersed in a thermostat at 28° C.

Two grms. of hide powder were weighed directly into each flask, and 250 cc. of salt solution, containing ten grms. of sodium chloride per litre, added. The flasks were then rotated for one hour, in order to insure perfect and uniform soaking of the material. Then the strong tan solution was introduced. The actual amount of tan liquor added is of little import, since interest centres only around concentrations at equilibrium, and the solutions were all to be analysed at a later stage. The volumes varied roughly from 1 to 25 cc. Since it was highly necessary to hold the salt concentrations in the various flasks constant, the tan liquor added was in every instance diluted to 25 cc. Thus in the case of the flask to which 10 cc. of strong tan solution were to be added, 15 cc. of distilled water were mixed with the chrome liquor before the latter was added to the tan flask. The conditions in all flasks were therefore the same, except for varying amounts of tan liquor.

The tanning process proper was run for four hours. Preliminary experiments showed that equilibrium was fully established in that time. Two grm. portions of hide powder were soaked one hour, then tanned for varying times, using in each instance 20 cc. of strong tan solution. At the end of each hour a flask was removed, and the solid phase analysed. The results are shown in Table I.

TABLE I.

Hours in contact with tan liquor.	Weight Cr_2O_3 in solid phase.
1	0·1795
2	0·2038
3	0·2093
4	0·2120
5	0·2115
6	0·2117

It will be noticed that after four hours there was a loss in the weight of Cr_2O_3 found. This may be attributed to experimental error, or it may be caused by disintegration and solution of the finer particles of tanned powder after so long a time in the rotating device.

The separation and analysis of the different phases under consideration presented by far the most difficult and perplexing problem. In order to obtain concordant results, there must be no solution adhering to the tanned powder, and the latter required quantitative treatment. Once tanned, however, hide powder is not difficult to operate upon; it does not tend to stick to chemical glassware, neither does it present serious difficulties in filtration. However, the removal of adhering solution requires the utmost care. Washing with any solvent whatever is entirely impossible; hence some simple method of mechanical separation was desired. The author believes that the problem was solved, within reasonable limits of error, by first filtering off the solid phase, then removing the adhering liquid with a centrifuge. Had it been possible to use the centrifuge alone, more accurate results might have been secured, because the uncertain amount of chromium adsorbed from the solution by the filter paper would have been eliminated. Unfortunately, when one attempted to run the solution containing the tanned powder directly into the centrifuge while it was rotating small particles of leather clogged the orifice.

A number of methods for obtaining a rough separation, giving a solid-liquid mixture of sufficiently small volume to be introduced into the stationary centrifuge, were tried; but the only successful one consisted in filtering off the solid phase on small four centimetre Büchner funnels, using hardened filter paper, and removing the last particles of tanned powder from the Erlenmeyers by washing with some of the solution which had already been through the filter. This rough separation could easily be effected in twenty minutes. The liquid at this point was saved for analysis. The solid phase still contained considerable solution, but the maximum amount of this could now be removed with the centrifuge. The latter with the usual Dulin Rotarex laboratory type. Each sample, after being carefully separated from the small disc of filter paper, was centifuged thirty minutes, at the maximum speed; and at the end of that time the assumption had to be made that they were uniformly dry. It has been pointed out by Leighton (*Jour. Phys. Chem.*, 1916, xx., 47) that where one is dealing with dilute solutions the nature of an adsorption curve is changed but little, when there is a marked difference in the amount of water adsorbed by the solid phase at different concentrations of the liquid phase. Since extreme care was exercised in the centrifugal process in order to secure uniformity of drying, it was not deemed advisable or necessary to determine the actual amount of water taken up in every instance.

The concentration of chromium in the solutions at equilibrium was determined volumetrically. The chromium in aliquot portions of each solution was oxidised by boiling with sodium peroxide, and converted into sodium dichromate with acid. A measured excess of tenth normal ferrous ammonium sulphate was run in, and the unoxidised iron determined with tenth normal dichromate, using diphenylcarbaside for indicator (*Jour. Am. Chem. Soc.*, 1913, xxxv., 156.

These concentrations represent true values at equilibrium, except for the small amounts of chromium solution adsorbed by the filter papers in the Büchner funnels.

Analyses of these papers showed the amount of water, and chromium, taken up by so small a disc to be entirely negligible when compared to the large volume of solution (275 cc.) dealt with.

In Table II., concentrations of the solutions are expressed in terms of the number of cc. of tenth normal ferrous ammonium sulphate equivalent to the dichromate from 100 cc. portions of the liquid phase.

At first the chromium in the solid phase was determined as follows:—The tanned hide powder was dried at 80°, pulverised, and fused with sodium peroxide, in nickel crucibles. The resulting mass was next dissolved in boiling water, acidified, and filtered. The chromium, now present as sodium dichromate, was determined by titration, as in the case of the liquid phase samples. But the quantitative fusion of so large a mass of tanned hide powder was found to be entirely too uncertain and troublesome, so a more simple method of analysis was devised. The dried product from the centrifuge was treated with a few cc. of nitric acid, placed in porcelain crucibles, and ignited at dull red heat in an electric furnace. This treatment burned out the gelatine of the hide, leaving behind the chromium oxide, sodium chloride, potassium sulphate, and the ash of the hide powder. The sodium chloride and potassium sulphate were washed out and the residue weighed. This, minus the weight of the insoluble ash from two grms. of hide powder was called Cr_2O_3. In Table II., the concentration of chromium in the solid phase is given in grms. of Cr_2O_3 taken up by two grms. of hide powder.

Concentration values for both the liquid and the solid phase are given in Table II.

TABLE II.

Concentration in liquid phase cc. *n*/10 $FeSO_4$ equivalent to dichromate produced by chromium in 100 cc. solution.	Concentration in solid phase grms. Cr_2O_3 adsorbed by 2 gms. hide powder.
0·08	0·0743
0·17	0·0873
0·43	0·1093
0·78	0·1238
1·49	0·1421
2·09	0·1591
3·12	0·1740
4·78	0·1940
6·29	0·2041
8·05	0·2120
11·37	0·2244
14·90	0·2352

When plotted, the result appears in Fig. 1.

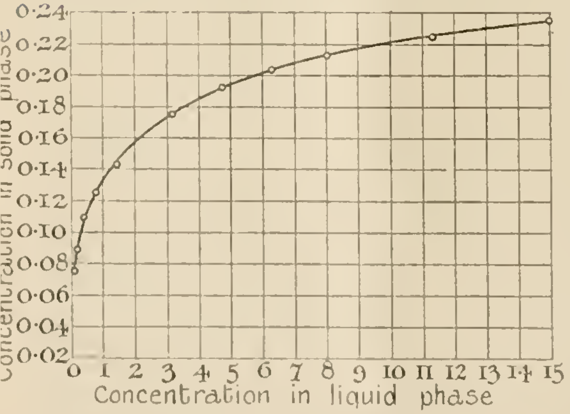

FIG. 1.—ADSORPTION OF CHROMIC ACID BY HIDE POWDER.

An inspection of the curve will reveal the fact that no breaks, horizontals, or vertical portions exist. The phase rule therefore tells us that we are dealing with an adsorption isotherm; and that no compounds between the hide powder and the tanning agent have been formed. In the case of chrome tanning, therefore, the contention of the physical theorists, that the first step is one of pure adsorption, has been verified.

The author desires to express his appreciation to Professor W. D. Bancroft for certain suggestions; and to Mr. E. K. Files, of this laboratory, for carrying out the analyses of the solid phases.—*Journal of Physical Chemistry*, xxi., No. 3.

INDUSTRIAL RESEARCH IN THE UNITED STATES.*

By A. P. FLEMING, M.I.E.E.

THIS paper is the first of a series which the Advisory Council for Scientific and Industrial Research intend to issue. Its purpose is twofold: primarily, to record the author's observations during his recent visit to the United States; secondly, to afford material for the consideration of the position of the United Kingdom in respect of Research.

Industrial Research in the United States may be classified according to whether it is undertaken by—Manufacturing Corporations (Companies); Associations of Manufacturers; Universities and Colleges (including the Mellon Institute of Industrial Research); National Institutions; Commercial Laboratories; Scientific Societies.

Amongst the companies which undertake research on an extensive scale are many whose products are well known in this country. For example, the Eastman Kodak Company spends on Research about £30,000, or 0·7 per cent of the Company's profits per annum; the General Electric Company from £80,000 to £100,000 per annum.

The most striking features of the research work undertaken by such firms are (i) the installation in many cases of full scale manufacturing facilities, which on the one hand enable processes to be perfected and the works to be relieved of the hampering effects of experimental developments, and on the other hand give the laboratory staff some elementary practical introduction to the complexities of actual manufacture as contrasted with the relative simplicity of laboratory preparation; (ii) the provision of manufacturing facilities in the laboratory in order to develop such products as result from new discoveries to the point at which the scale of manufacture calls for transfer to one of the works departments or to a new or separate organisation; (iii) the growing tendency to devote more and more of the resources of the laboratories to pure science investigations with a view to making discoveries. Such discoveries produce industrial developments which will facilitate progress in industries already established, or secure priority in some new industrial field.

Other noteworthy facts are the freedom with which results in pure science are published; the growing appreciation in the factory of the commercial value of scientific men; the recognition of the value of research laboratories as a means of inspiring confidence in the minds of customers; in short, the report makes it manifest that science pays.

There are a number of Associations of Manufacturers which undertake research work for the common benefit of their members. In some instances the work is carried out in laboratories connected with individual manufacturers, in Universities, or at the Bureau of Standards. Some associations, for example, the National Canners' Association, possess their own research laboratories.

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The research work of the Universities and Colleges presents many interesting features, prominent amongst which are the establishment, in conjunction with the industries concerned, of experiment stations where large scale investigations of immediate industrial interest can be carried out, and the endowment of fellowships by firms and by scientific societies.

The Mellon Institute is unique in character. Built, equipped, and endowed by the Mellon Brothers, it is affiliated to the University of Pittsburgh. It contains about thirty laboratories in which work is carried out on behalf of manufacturers, who are required to endow fellowships for a period of one or more years for as many men as are needed to carry on the proposed investigations, the general direction of which is in the hands of the permanent staff of the laboratories. When a research is nearing successful completion in the laboratory, it is usual to erect a unit plant on a small manufacturing scale in order to develop the process fully before it is attempted on a commercial scale in the works. The results of the research are not published until at least three years after the investigation, except by consent of the manufacturer on whose behalf the work was undertaken. The permanent staff also carry on their own researches, the results of which are published in the technical press.

The National Institutions which deal with industrial research are lavishly financed either by the State or by private benefaction. Most excellent means for publishing their results have been developed; they offer extensive acilities to industry for research; and their advice is reely given. The work done by such Institutions as the Bureau of Standards, the Carnegie Institution, the Forest Products Laboratory, and the Bureau of Mines is well known in this country.

The Commercial Research Laboratories are on an extensive scale and are well equipped. The Scientific Societies, in addition to offering channels, in their journals, for the publication of Research results, are also in some instances interested in, or are in control of, endowment funds for Research Work.

The development of Research by individual firms, or by scientific or industrial organisations, has been stimulated by the appreciation of the progress achieved in Europe, especially in Germany, by similar means, and also by a growing anxiety to conserve the national resources.

Little has as yet been done to prevent overlapping by the various Research Agencies, but some attempt at co-ordination must inevitably be made, and an important influence in this direction is the growing appreciation of the possibilities of export markets and the need to combine manufacturing facilities in order to meet international competition effectively.

Furthermore, every sort of encouragement is given to students to take up Research Work and much care is expended on their training in close contact with industry. It is also worthy of note that in the United States important investigations have been successfully dealt with by men of average ability working under competent direction. In this country, on the other hand, where there is no deficiency of intellectual ability for Research, the impression seems to prevail that important investigations can only be made when the worker is a man of outstanding genius unhampered and undistracted by association with industry; as a consequence there is a lack of organisation whereby scientific knowledge may be turned to industrial account.

Reference has already been made to the value of the results of organised research as a factor in the struggle for world markets, and the importance to this country of this aspect of the question is strongly urged in the Section (XIV.) of the Report entitled "Some Fundamental Considerations."

The War has disclosed in British Industry an enormous latent capacity for adaptability to entirely new lines of manufacture, many of which have depended for their development upon scientific research. The research facilities are, as yet, disproportionate to the need, and there is an urgent call for the establishment of an organisation which shall maintain the creative impulse given by the war.

In the light of his study of American developments Mr. Fleming suggests that the most important alternative schemes for the United Kingdom are:—

(*a*) Research Laboratories in industrial works.
(*b*) Research Laboratories for a group of works in the same industry.
(*c*) The centralisation of research in the Universities or Colleges.
(*d*) An Imperial centralised laboratory for the whole industry.

Mr. Fleming adds that, in considering these policies, i is imperative to bear in mind that industry is the basis of national prosperity and that every resource should be used to facilitate its progress.

AN APPARATUS FOR THE REDUCTION OF VOLUMES OF GASES TO STANDARD TEMPERATURE AND PRESSURE.

By A. V. C. FENBY.

THE apparatus to be described has been designed to facilitate the reduction of the volumes of gases, measured at known temperatures and pressures, to volumes at 0° C. and pressure of 760 mm., and to effect a saving in the time usually spent on these calculations. A direct reading instrument for this purpose should be of considerable service in the laboratory.

If the volume of a gas, measured at t° C. and under a pressure of P mm, is $_pV_t$, then the volume at 0° C. and under pressure of 760 mm. is—

$$_{760}V_0 = {}_pV_t \times \frac{273}{(273+t)} \times \frac{P}{760}.$$

The apparatus is designed to measure the factor,—

$$\frac{273}{(273+t)} \times \frac{P}{760},$$

by which the volume $_pV_t$ is to be multiplied to reduce it to volume at 0° C. and 760 mm. pressure, this factor being read off directly from the apparatus.

The apparatus can also be used to calculate the volumes of gases (*a*) when heated t° C. at constant pressure, (*b*) when submitted to a change of pressure at constant temperature, or (*c*) when heated to temperature t° C. and submitted to a pressure P mm. after measurement at 0° C. and 760 mm. pressure.

Several forms of the apparatus are shown in Figs. 1, 2, and 3. A description of the construction and method of using these forms will now be given.

The apparatus shown in Fig. 1 consists of a horizontal arm, A B, to which is attached a vertical arm, C D. The arm, C D, is hinged to the slide, *a b*, which moves along A B, and can be clamped in any position on A B. When not in use, C D is shut down along the upper side of A B. A third arm, E F, is fixed to A B, and turns about the end, E. This arm can be clamped in any suitable position by the screw, G, which moves along the slotted arm, H. The outer portion of the arm, E F, is enlarged, and carries a transparent scale with a centre line, *f g*, ruled on it. This scale serves as a cursor, and the arm, E F, will be called the "cursor-arm.

The arm, C D, is provided with two scales; the scale, V V, on the left is the "volume-factor" scale, and the scale, T T, on the right is the "temperature" scale; this is graduated in °C. from 0° to 100°, and from 0° to −273°, or in absolute temperatures from 0 to 373°. The figures are not shown in the drawing. The scale, V V, is marked 1·0 at the point where the line *f g* cuts it, when the line *f g*

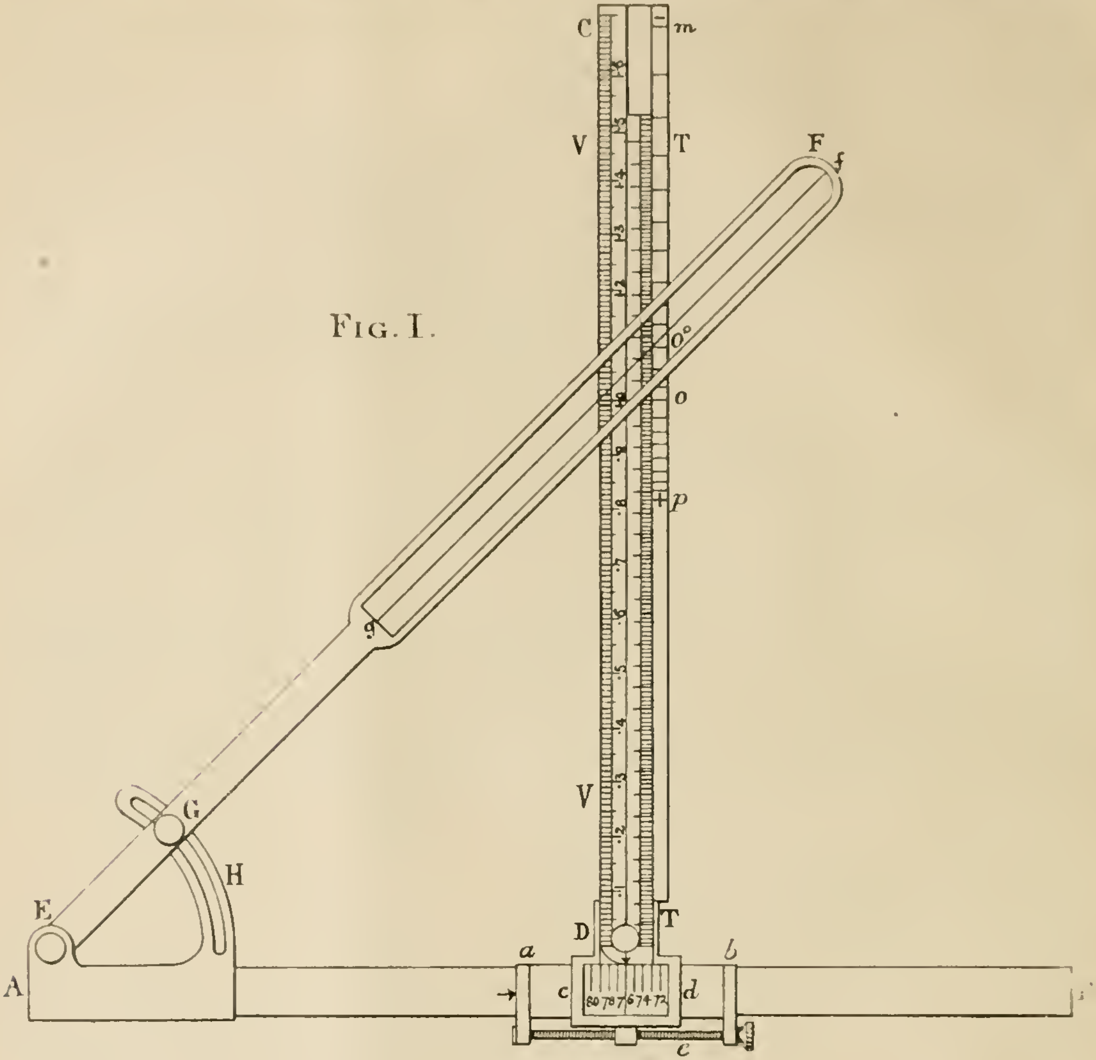
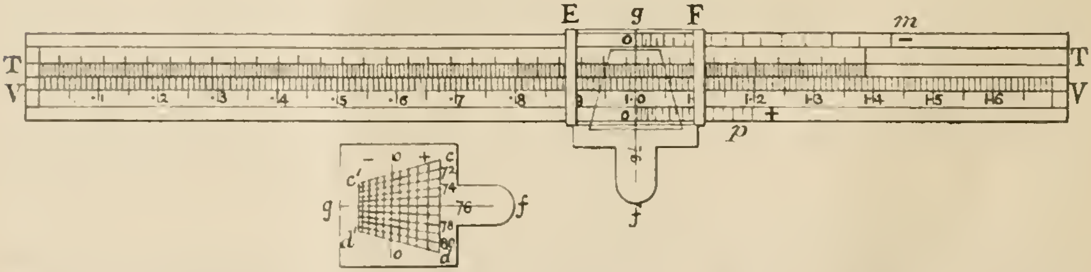


FIG. I.

FIG. II.



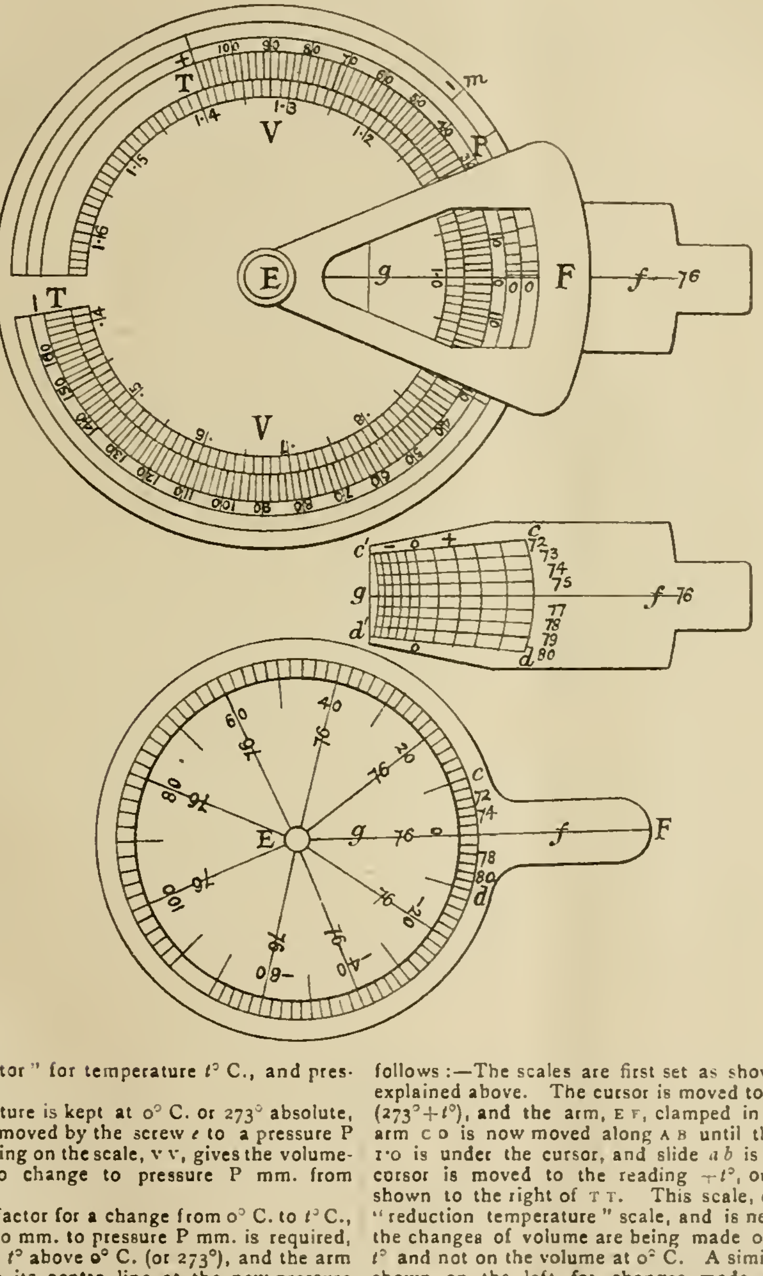
passes through temperature reading 0° C., or 273° absolute, and is graduated to read from 0 to 1·7 in hundredths of the unit volume, as shown in the figure.

The slide, *a b*, which moves along the arm, A B, is provided with a pressure scale engraved on it, and showing differences of pressure of 10 mm. between 720 mm. and 800 mm. The centre line of the arm, C D, can be moved along this pressure scale by means of the screw, *e*, which moves the carrier, *c d*, to which C D is fixed. The arm, A B, will be called the "pressure" arm, and the arm C D the "temperature" arm.

To use the apparatus the temperature arm, C D, is set with its centre or "zero" line over the reading 760 mm. on the pressure scale, and the slide, *a b*, is moved to the position indicated by the index, *i*, on A B. The cursor is then set to the temperature 0° C., or 273° on scale T T. The volume factor is 1·0, as shown in Fig. 1.

(*a*) If the cursor is moved t° above 0° C. or 273° absolute, the pressure being unchanged, the cursor will give the "volume-factor" for temperature t° C., and pressure 760 mm.

Fig. II.



(*b*) If the temperature is kept at 0° C. or 273° absolute, and the arm, C D, is moved by the screw *e* to a pressure P mm., the cursor reading on the scale, V V, gives the volume-factor at 0° C. to change to pressure P mm. from 760 mm.

(*c*) If the volume-factor for a change from 0° C. to t° C., and from pressure 760 mm. to pressure P mm. is required, the cursor is moved t° above 0° C. (or 273°), and the arm C D is then set with its centre line at the new pressure P mm. The cursor reading on the scale, V V, now gives the required volume-factor. Suppose we require to find the volume-factor for a change from 0° C. to 15° C., and from pressure 760 mm. to pressure 750 mm. The cursor is set to the reading 15° C. (or 288°), and the volume-factor reading is 1·056 (factor for temperature change only at pressure 760 mm.). The arm, C D, is now set to the new pressure 750 mm., and the volume factor becomes 1·070.

(*d*) The reduction of the volume of a gas measured at temperature t° C., and under a pressure of P mm. to its volume at 0° C., and pressure of 760 mm., is effected as follows:—The scales are first set as shown in Fig. 1 and explained above. The cursor is moved to the temperature ($273^\circ+t^\circ$), and the arm, E F, clamped in position. The arm C D is now moved along A B until the volume-factor 1·0 is under the cursor, and slide *a b* is clamped. The cursor is moved to the reading $+t^\circ$, on the scale *o p*, shown to the right of T T. This scale, *o p*, is called the "reduction temperature" scale, and is necessary because the changes of volume are being made on the volume at t° and not on the volume at 0° C. A similar scale, *o m*, is shown on the left for changes made at temperatures below 0° C. These "reduction temperature" scales are marked respectively + and −. In the figure the graduations are only shown for every 10° and are not numbered. When the cursor has been set to t on the "reduction temperature" scale the reading on V V is the volume factor to reduce volume to 0° C. at pressure P mm. The pressure is now changed to 760 mm. by moving C D along the pressure scale, and the volume-factor required is read off. An example will make this clear. A volume of V cc. of gas, measured at 30° C. and under a pressure of 720 mm., is to be reduced to volume at 0° C. and 760 mm. The apparatus being set as shown in Fig. 1, the cursor is set to temperature reading 273° + 30° = 303°, and the arm C D moved inwards until the volume factor is 1·0, and then the arm E F is moved down to 30° on the + "reduction temperature" scale, op. The volume-factor is now 0·900 (for volume at 0° C. and pressure of 720 mm.). The arm C D is now set at pressure 760 mm., and the volume-factor is now 0·853. Therefore V cc. × 0·853 will give the volume at 0° C. and 760 mm.

By means of an additional arm between C D and E, and parallel to C D, graduated from 0 to 100, the apparatus can be used to calculate percentage compositions and results of combustion experiments. This arm is not shown in Fig. 1. The extra arm, in conjunction with an additional scale along the arm A B, can be used to find "*weight-factors*," by which the weights of volumes of gases, measured at t° C. and pressure of P mm., can be found by multiplying the measured volumes by the "weight-factors."

In Figs. 2 and 3 modified forms of the apparatus are shown. Fig. 2 shows the apparatus arranged on the slide rule pattern. The corresponding parts are denoted by the same lettering in all the figures. The temperature scale, T T, and the factor scale, V V, are arranged side by side, but *one* of them is movable, parallel to the other, preferably the scale V V. The cursor carrier, E F, moves along the scales, as in a slide rule. The cursor, $cd, c'd'$, is shown separately for clearness; fg is the 760 mm. pressure line, and the other pressure lines are slightly divergent, and are crossed by the zero temperature line, O O; other temperature lines are drawn parallel to line O O, and correspond to temperature intervals of 20° between + 100° C. and − 100° C. The scale $cd, c'd'$ moves horizontally in the carrier E F, and thus any required temperature line can be set over the factor scale, V V. The "reduction temperature" scales, marked + and −, are placed on opposite sides of the apparatus.

Fig. 3 shows a circular form of the apparatus. The factor scale, V V, is shown inside the temperature scale, T T, but the reverse arrangement may be adopted; one of these scales is movable, preferably the outer one, which is usually T T. The "temperature reduction" scales are marked on the same scale as that on which the temperatures are marked, and move with scale T T if this is movable. The cursor-carrier, E F, revolves round the centre E, and the cursor scale, which is similar to that of Fig. 2, moves horizontally in a slide in the carrier, E F, which can be clamped in position by the screw, E. The circular cursor, shown below Fig. 3, may replace the sliding cursor described above. The pressure scale, cd, from 720 to 800 mm. is marked in *separate* segments for intervals of temperature of 20° C. between 0° C. and + 100° C., and 0° C. and − 60° C.

The method of using these forms is similar to that described above for the original form; when a change of pressure is to be made at a temperature t° the cursor is set with the temperature line t° along the edge of the scale, V V, before the pressure change is made.

In the apparatus as described the temperature range extends from 0° absolute temperature to 373° absolute, but for most purposes a more limited range would be sufficient. The range of the apparatus, both as regards temperature and pressure, may be easily extended much beyond the above limits without enlarging the apparatus.

The Whitgift School, Croydon, May 9, 1917.

THE REALITY OF ATOMS.

By A. FINDLAY, M.A., D.Sc.

At a time when the purely utilitarian applications of physical science occupy, not unreasonably, a chief place in men's minds, it is well to turn aside occasionally to the contemplation of other aspects of science and to consider some of the triumphs which have been won in the domain of pure knowledge. The man of science is no mere dealer in "cold facts," no mere gatherer of stones by the wayside of life; but he seeks also, by the divine gift of an intuitive intelligence, "to explain the complications of the visible in terms of invisible simplicity." It was to such intuitive intelligence that we owe the Atomic Theory, put forward by the Manchester schoolmaster, John Dalton, in the early years of last century—a theory which recently formed the theme of the presidential address to the Chemical Society. Although the march of knowledge has carried us far from the point where Dalton stood, the theory which he propounded still remains the essential basis of modern physical science.

From the earliest dawn of thought men's minds have been busied with the question of the constitution of matter; and throughout all time one has had to decide between the two alternatives of continuity and discontinuity. With the speculations of the ancient Greek philosophers (grand and comprehensive as they often were), with the Aristotelian doctrine of the four elements (based on the Empedoclean conception of a continuous primordial matter), or with the Atomic Theory of Leucippus and Democritus—we need not longer delay. They helped but little, if at all, towards the explanation and co-ordination of the facts of science. However much the idea of continuity appealed to the older thinkers, in modern times it has come to be recognised that "the notion of continuity is the result of an arbitrary limitation of our attention to a part only of the data of experience." The further we extend our investigations, the more refined and powerful the instruments we employ, the more does the coarse grainedness of matter become evident. Apart from the conception of discontinuity the atomic theory of Dalton had nothing in common with the ancient philosophy so admirably expounded by Lucretius. In the older theory the atoms were all regarded as consisting of the same primordial material, although differing in size and shape; but to Dalton the atoms differed in their nature. In the case of any particular element, the atoms were assumed to be all exactly alike in their properties, including their mass, but they differed from the atoms of any other element. At first no distinction was made between the smallest particle of an element and the smallest particle of a compound, and a certain amount of difficulty and confusion was thereby caused, for it is clear that, although we may regard the atom of an element as indivisible, the atom of a compound must be capable of being broken up into the atoms of its component elements. A new name was therefore introduced by the Italian chemist Avogadro, who called the smallest particle of a compound a molecule, and for the advance of chemical science this new conception has been of inestimable value.

The theory of Dalton, we have seen, postulated definite properties for the atoms of the elements, and consequently the atom of an element must have a definite mass or weight; and the determination, not of the absolute mass but of the relative masses or weights of the atoms, became one of the main preoccupations of chemists in the first half of the nineteenth century, and still forms the subject of exact investigation. It was, in fact, just because Dalton's theory was capable of quantitative expression in terms of the relative weights of the atoms of the different elements that it was possible for the hypothesis of the atomic constitution of matter to become for science the invisible simplicity behind the complications of the visible. But is it anything more than an hypothesis, useful but not necessarily representing actual fact? Recent discoveries in science allow us now to answer this question with confidence. They have, from several different directions, contributed towards establishing the atomic hypothesis in a position of unassailable strength, and have furnished a proof of the real and actual existence of atoms or discrete particles as constituting the fundamental basis of matter. Only a few of these proofs can be indicated here, but a clear account of the evidence accumulated in support of the real existence of discrete particles has recently been published by one whose work has greatly advanced our knowledge of this subject ("Atoms," by Jean Perrin).

The phenomena of diffusion, more especially in gases, led to the conclusion that the particles or molecules of which matter was assumed to be constituted are not in a state of rest. In the case of a gas, these molecules are regarded as being in a state of constant and tumultuous commotion, which is not entirely subdued even when the gas is condensed to the liquid, or frozen to the solid state. That, at least, is the picture of matter which presented itself to the inner vision of a genius like Clerk Maxwell, and which forms the basis of what is known as the kinetic theory, a theory which was developed by applying to these still hypothetical molecules the general laws of mechanics. In this way it became possible, on the basis of experimental data, to calculate not only the absolute mass of the molecule—the hydrogen molecule weighs about three quadrillionths (million million million millionths) of a gramme—but also its dimensions (approximately one hundred millionth of an inch in diameter), and the speed of its movement (several hundred yards per second); and the agreement between the values derived from the different kinds of measurement cannot but excite our admiration. And yet the theory cannot carry complete conviction, by reason of the number of hypotheses which it involves; and so there have not been wanting some who refused to accept the objective reality of molecules. And yet, even in 1827, these molecules had, all unknown to their observers, made their presence manifest by the effects which they produced. In that year the botanist, Brown, observed that when suspensions of pollen grains were examined under the microscope the particles were seen to be in rapid motion, vibrating, rotating, moving along a zigzag path, sinking, rising—perpetually in motion. In this so-called Brownian movement—observed long ago by Buffon and Spallanzani, who saw in it a manifestation of life—we see, not, it is true, the molecules themselves, but the effects of the incessant bombardment of the coarser particles of the suspension by the molecules of the liquid. When one applies to the suspension the law of the equipartition of energy, it follows that, in a condition of equilibrium, the kinetic energy of the relatively coarse particles will be the same as that of the molecules of the liquid. We have, then, in the Brownian movement merely a magnified picture, as it were, of molecular movement; and if this is so, then the magnitudes calculated from these comparatively coarse suspensions should be the same as those calculated according to the molecular kinetic hypothesis. This conclusion has been tested in various ways, more especially by the French physicist, Jean Perrin, and has been found to be correct.

As a result of the combined action of gravity and of the kinetic energy of the molecules, the molecules in a column of gas are more crowded together at the bottom of the column than at the top, in accordance with the law that when the distances from the bottom increase in arithmetical progression the concentration of the particles diminishes in geometrical progression. By counting the number of particles at different levels of a column of a fine suspension of gamboge in water, Perrin found that the distribution of the particles accurately obeyed the same law. These particles in Brownian movement, therefore, behave exactly as the molecules of a gas would behave according to the kinetic theory; and in a number of other ways also the suspensions of particles which can be seen behave in exact concordance with the laws which have been deduced for invisible particles. Our belief in the actual existence of these particles is thereby greatly strengthened. The extension of our limits of vision, also, which the invention of the ultramicroscope has made possible, has disclosed the existence of particles in what hitherto had appeared, even under the most powerful magnification, to be homogeneous matter; and by this means particles not greatly exceeding in dimensions those of the molecules have been detected. The smaller the particles the more lively is their motion, so that we can scarcely hesitate to believe that in the rapid, darting motions of the ultramicroscopic particles we have made manifest to us something of the extraordinary stir and commotion which is going on in that world of molecules which is beyond the power of our direct observation.

But the grained or discontinuous structure of matter has been still more clearly demonstrated in the recent striking work on radio-activity. The phosphorescent light emitted by certain materials, when bombarded by the α rays emitted by radio-active substances was found by Sir William Crookes to be resolved, when examined by a magnifying glass, into separate scintillations or points of light, each of the star-like points of light marking the impact of a projectile; and in the spinthariscope, invented by Sir William Crookes, one is enabled to see the individual effect of a single atom. But these α-rays, as Sir Ernest Rutherford most definitely has shown, are positively charged atoms of helium, which he has even succeeded in counting, and the atomic structure of this gas is thereby demonstrated.

Whether we calculate the fundamental molecular magnitudes from the viscosity of gases; from the Brownian movement of fine, but visible particles; from the phenomena of radio-activity; or from the blue colour of the sky, by which also the discontinuous structure of matter is made manifest, the same results are obtained, and the real existence of molecules is thereby established with a probability amounting to a certainty. But while we can regard the atomic constitution of matter as established beyond any reasonable doubt, yet, in the words of Prof. Perrin: "Atoms are no longer eternal indivisible entities, setting a limit to the possible by their irreducible simplicity; inconceivably minute though they be, we are beginning to see in them a vast host of new worlds. . . . Nature reveals the same wide grandeur in the atom and the nebula, and each new aid to knowledge shows her vaster and more diverse, more fruitful and more unexpected, and, above all, unfathomably immense." – *The New Statesman*, June 16, 1917.

NITROGEN FROM THE AIR.

Manchester's New Enterprise.

We are able to supplement from a well-informed source the interesting announcement in the *Manchester Guardian* of June 23 that plant is about to be erected in Manchester for the manufacture of nitrogenous products from the nitrogen in the air. For reasons that will be obvious, fuller details must be reserved until the conclusion of the war.

Ever since the British blockade was enforced, Germany has found it impossible to import Chilian nitrates for the manufacture of explosives and fertilisers. It reverted, therefore, to the expedient of "fixing" the nitrogen from the air, and has adopted it to a huge extent since almost the beginning of the war. It has been stated in German technical journals that the output of nitrogenous products by the Badische-Anilin Fabrik, with the aid chiefly of the Haber-catalytic process, amounts now to about 500,000 tons a year. By these means the Germans get all the nitrogenous ingredients for their high explosives.

Attempts have been made to work the Haber process in this country, but all have failed, and the general consensus of opinion now is that this is not a commercial process, as the expense and risk appear to be enormous. With the Germans, however, it is a case of needs must.

The only other way by which nitrogen can be fixed from the air is by the electric processes, of which up to now the principal have been the Baekeland and Evde, the Schönhurr, and the Pauling. All of these are single-phase and electrical processes, and are considered workable commercially only in places like Norway, where electricity can be generated cheaply by water power. None of them has been worked in England, because of the high cost of electricity here, which makes them uneconomic under ordinary conditions.

The consequence is that the fixation of atmospheric nitrogen has not been adopted in this country, which relies for its supplies of this valuable ingredient of high explosives and an indispensable part of all the principal fertilisers on the utilisation of Chilian nitrates, the price of which has increased enormously since the beginning of the war.

A New Process: English Discovery.

A new factor in the situation has now arisen in the new method of nitrogen fixation from the air which is about to be started in Manchester. National considerations preclude details being given at present, but it is believed that with this process nitrogen can be "fixed" anywhere in England at a very low cost, even where electricity is fairly expensive, because it apparently achieves the highest efficiency of nitrogen fixation per kilowatt hour of energy used that has ever been achieved or even dreamt of by any of the other processes mentioned. Its inventor is a British subject.

The Manchester Corporation succeeded in being the first to get the industry started, because it went out of its way to help the promoters, the International Nitrogen and Power Company, 8, Waterloo Place, London, who hold the exclusive rights to work the process in Great Britain.

The new industry is believed to have great possibilities, not only for war purposes but after the war. Possibly when the method comes to be worked throughout the United Kingdom it will make this country independent of oversea supplies of fixed organic nitrogen, and provide a new security against the danger of interruption of oversea supplies of essential ingredients of explosives in time of war. If it can be done the whole of our nitric acid supplies could be obtained in this way, and also picric acid, an essential ingredient in synthetic dyes.

Above all, it would bring to realisation Sir William Crookes's prediction to the British Association at Bristol over thirty years ago that the future of the white race would largely depend on the economic fixation of atmospheric nitrogen, by which the world might be made to yield larger quantities of wheat and other foodstuffs.

Through the good offices of the Manchester Corporation an excellent site for the works has been provided. Construction has already begun, and the establishment should be working within six months from now.

There is no special virtue in the air of Manchester that has led to the selection of the city for this important pioneer enterprise. The choice was determined by other circumstances. Nor need the public have the least apprehension of the effects of the process on atmospheric conditions. The volume of air used up is an infinitesimal fraction of the aerial ocean.

Inquiries made recently by a representative of the *Manchester Guardian* showed that a movement for carrying into effect a project for obtaining nitrates from the atmosphere was started in Manchester ten or twelve years ago, the motive being, of course, mainly a commercial one. The promoters were, for the most part, engaged in the bleaching industry, who desired to avoid, if it was possible, the expense of bringing nitrates so largely used in their business from South America. It was found, however, that an obstacle to the development of that scheme was the intense heat required to make the process successful. "We needed heat," one of the promoters of that time said recently, "of an intensity of 2000°, and the result was that the whole of the ovens and appliances necessary were destroyed before it could be attained. Another obstacle was placed in the way by the shipping trade, who feared the loss, if the experiments then made proved a success, of the nitrate shipping trade. Means were subsequently found of overcoming the difficulty created by the intense heat required, and further efforts were made in France which proved to be successful. There is a works in that country now which has for a number of years been producing nitrates from the air."

A chemist at a large house in the dyeing trade expressed the view recently that but for the fact that the Germans had for years obtained nitrates from the air the war would have been over long ago, considering the present difficulties in the way of their obtaining them from Chili or other South American sources.

MAKING ANIMALS TRANSPARENT.

What the Royal College of Surgeons has to say to the Spalteholz Method.

(*From a Correspondent*).

In the Chemical News of June 13 appeared an account of the Spalteholz method of making animals transparent, as exemplified in successful specimens exhibited to a Chemical News representative by Dr. S. F. Harmer, F.R.S., at the Natural History Museum, South Kensington.

When Dr. Harmer applied to the Patents Court for licence to employ this method, which is covered by a German patent, the Controller of Patents, Mr. Temple Franks, threw doubt on the validity of the patent because, apparently, it seeks to patent a principle of optics by basing the method on the refraction of light. The dead animal, after chemical treatment, is placed in a solution having tho same index of refraction as its own tissues. Skeleton, muscles, and arteries are then revealed through the fabric of the outer tissues.

At the Royal College of Surgeons, however, doubt is cast on the subject matter of the patent from another point of view—that fruitful source of contention known, in the term of the lawyers, as prior user! In a word, there is nothing new in the method at all! They have used it at the Royal College of Surgeons for years!

Prof. Keith (who sat with the imposing skeleton of the Irish giant O'Bryne behind him—an eighteenth century worthy who looked out on the world from the unusual altitude of 8ft. 4in.) assured the Chemical News interviewer that the idea of clarifying tissues was as old as the hills. Instead of applying the process to a small piece of tissue Spalteholz had used it for large bodies—"a thing none of us have wanted to do particularly," said Dr. Keith, "because we don't see much use in it. It has long been used in microscopy. Indeed, the principle of the employment of clarifying oils is tolerably obvious. You go into a wooden building, in the daylight, and you see the sun shining through a resinous knot—and there you are, the whole thing is complete! The rat, by this process, is transparent, instead of the knot, because of an essential oil.

"But Spalteholz cannot claim to have invented transparencies, even of animals. Thoy were first made in the fifties by Prof. Beale, of King's College, in the Strand. Beale used as alkali—potassium hydrate will serve—though Beale never patented his method. He was too busy with other things. Beale's method was afterwards re-discovered on the Continent, where it came to be known as Schultze's method. We have employed Beale's method in the College for the last fifty or sixty years, and have several specimens in the museum.

"The Invisible Man."

"Spalteholz could not patent an absolute fact in the process of thought. The only thing he could patent would be some new medium. You could not patent embalming, for instance, though you might patent a bran-new way of doing it. The man who tried to patent anything else would be a rotten bad scientist. We have human embryos up to five and six months in the museum, all as transparent as anybody could wish—they were prepared by my colleague Mr. Burne.

"By the bye, had not you better see Mr. Burne," Prof. Keith went on. "As for picking out any system for special study, it is always possible to use a nerve stain or a cartilage stain. Anyhow, we have specimens going back to the earliest clarifying days—at any rate to the seventies. Spalteholz wss the first to apply the process to so large a body as the human heart. He examined the distribution of its arteries. He injected the arteries and veins and then clarified the heart. As for the rest, he has simply produced something unusual and pretty, but it is a source of no growth of knowledge."

Mr. R. H. Burne, when seen, had read the article in the Chemical News.

"So far as I know," he said, "Beale was the first to employ such a method in 1853. You will find a description of his process in 'Beale: The Microscope in Medicine,' 4th edition, 1878, pages 48 and 446. He used caustic soda as a clearing agent and employed the method for the demonstration of the developing skeleton of human embryos. Beale's method was elaborated later by Schultze (*Anat. Anzeiger*, 1897, vol. 13, Verhandl) and has since been carried to great perfection by Mall in America (*Am. Jour. Anat.*, 1906, V., part iv.)

"Clearing in essential oils, as done in the Spalteholz method, was used with success by the late Martin Woodward in about 1890-2, for the examination of certain mammal jaws, in the search for rudimentary teeth. He employed the usual microscopic clearing agents, particularly oil of cloves. The principle is worked out to its logical conclusion by Wells in his tale of 'The Invisible Man.'

"The advance on previous processes made by the Spalteholz method is to be seen in the more careful and scientific adjustment of the refractive index of the clearing agent to the refractive index of the tissue to be cleared. It is a refinement of method rather than a new method, and in certain cases, especially when the part treated has been injected with an opaque substance, gives very excellent results."

Mr. Burne, who was himself engaged on the investigation of mammal jaws through transparent agency, led the interviewer into the basement of the College, where certain specimens have been wisely retired, to be out of the reach of air-raids, and there, in case after case, were displayed transparent objects. They were precisely the same sort of thing as the transparent rat at South Kensington, though the rat undoubtedly has the advantage in avoirdupois, density, and other "substantial" directions.

PROCEEDINGS OF SOCIETIES

ROYAL SOCIETY.

Ordinary Meeting, June 21, 1917.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

"*Revolving Fluid in the Atmosphere.*" By Sir Napier Shaw, F.R.S.

It is generally assumed, as appears particularly from a recent paper by Lord Rayleigh with reference to a former paper by Dr. J. Aitken, that the motion of air in cyclones and anticyclones may be classed as the motion of revolving fluid, symmetrical about a vertical axis. Reasons are given to show that this assumption with regard to cyclones and anticyclones of middle latitudes is erroneous; that circular isobars on the map do not indicate revolving fluid, and *vice versâ*, that travelling revolving fluid would not be indicated by a system of circular isobars.

The next point for consideration is how a mass of revolving fluid travelling with a speed of translation of the same order as the speed of rotation, and of sufficient size, would be represented on a map. Diagrams are drawn showing the distribution of velocity in four cases for different ratios of the velocity of translation to the velocity of rotation, and assuming that systems of velocities could be fitted to pressure lines of the same shape, it is inferred that cases of travelling revolving fluid would be indicated by isobars similar to those which are classed meteorologically as belonging to small secondaries, or distortions of the isobars, generally on the southern side of the great cyclonic systems.

Conditions are next considered which must exist if a column of rotating fluid is maintained and transported within a current represented by the isobars of a great cyclonic depression. The conditions arrived at are briefly:—

1. That the velocity of translation must be the velocity corresponding with the separation of the isobars of the main depression unaffected by the presence of the revolving mass.

2. The column must probably extend throughout the troposphere, otherwise it could not be "capped."

3. The velocity of the current transporting the revolving fluid must be the same at all heights. This condition is shown to be satisfied if the line of lapse of temperature with height in the atmosphere corresponds with an adiabatic line, and this is known to be approximately the case in a cyclonic depression where convection has been ubiquitous and vigorous.

"*Absorption Bands of Atmospheric Ozone in the Spectra of Sun and Stars.*" By Prof. A. Fowler, F.R.S., and Hon. R. J. Strutt, F.R.S.

In this paper it is shown that a series of narrow bands in the ultra-violet absorption spectrum of ozone appears in the spectra of the sun and stars near the extreme end of the photographic spectrum. The atmospheric origin of these bands is proved by the increase in their intensity in the solar spectrum as the sun's altitude is diminished. The observations are considered strongly to confirm the view of Hartley that ozone is the constituent of the atmosphere which limits the spectra of celestial bodies in the ultra-violet.

SOCIETY OF GLASS TECHNOLOGY.

A joint meeting of the Faraday Society and the above Society was held in the Department of Applied Science at the University of Sheffield on Wednesday, June 20. Mr. W. F. J. Wood, B.Sc., was in the Chair.

Dr. William Ripper, Vice-Chancellor of the University, opened the meeting with a few words of welcome from the Applied Science Department. He spoke of the interest taken in both Societies by the University, the authorities of which were most anxious to further the well-being of the Societies by any means in their power.

Prof. W. G. Fearnsides, M.A., followed with an address on "*The Resources of Refractory Materials available for Glass Manufacture.*"

The problem of refractories was common to both the steel and the glass industries. In the manufacture of steel, furnaces were run at a much higher temperature than in the case of glass, and so from the point of view of withstanding temperature, a refractory useful in steel would be quite good for glass. In the manufacture of the latter, however, the severest test on the refractory was its power of withstanding chemical action.

Refractory substances are to be found in different geological formations, but it is worthy of note that many of the most used refractories are in the vicinity of coal measures. The occurrence and relative importance of various ganister and fireclay beds were discussed and their positions indicated on a large scale map. The resources of refractories in the West Riding of Yorkshire received particular emphasis, special mention being made of silica from Meltham, near Huddersfield, ganister from the neighbourhood of Sheffield, and fireclay from the Halifax district. The relative values of the "Wooden Box" clay from Church Cresley in the Leicester coalfield, of the clay from South Wales and from Glenboig in the south-west of Scotland, were also commented upon. An interesting and instructive address ended with a discussion of the kaolins and ball clays of Cornwall, Devon, and Dorset.

Mention should be made of a very representative collection of specimens of refractories which had undergone change in glass and steel furnaces. At the close of the meeting these specimens were the subject of an animated discussion among members. It is hoped that several of them will be available for future reference in the museum of the Society.

A second address on "*Refractory Materials*" was delivered by Mr. J. H. Davidson, M.Sc., of the Glass Technology Department of the University of Sheffield.

The analyses of various clays were given and their likenesses and differences were discussed. In addition, a stone from Durham used in building glass tank furnaces had been analysed, together with several similar local stones. The stones differed little amongst themselves in analysis, but were widely different from clay, as they contained considerably more silica and less alumina. Some most valuable information regarding the plasticity of various clays was imparted. It was shown that the percentage of water taken up by a clay in working was a measure of its plasticity, and methods of testing the plasticity of clay were given. From the numbers obtained it was found that "Wooden Box" (Church Gresley) clay was anomalous in its behaviour. The Leeds fireclay required 18 per cent of added water for plasticity, Halifax 18½ per cent, Stourbridge 18 per cent, Germany 19½ per cent, whilst "Wooden Box" required as much as 25 per cent.

The contraction due to drying and firing was next considered, and very useful data was given. Most clays contract 5 per cent to 6 per cent in drying, but "Wooden Box" is again unique, as it contracts 6½ per cent. The firing tests were carried out in two stages. First of all, the shaped blocks were fired at a temperature of 1000° C., when a contraction in length of ½ per cent to 1 per cent was noted, with the exception of "Wooden Box," which contracted as much as 11½ per cent. Under the same firing conditions the stones *increased* about 1 per cent in length. A second firing to 1450° C. was given, and the following total contractions were observed:—

	Per cent.
Halifax Clay	8¾
German Clay	10
Leeds Clay..	10
Stourbridge Clay	11
"Wooden Box"	17

At this temperature it was found that stones increased 3½ per cent in length.

In all the tests carried out it will be observed that "Wooden Box" clay is anomalous in its behaviour.

Since clays contract so much on firing the necessity for the admixture of "grog" in pot making is at once apparent. In the opinion of the author, the present day pot maker used too little "grog" and also "grog" of the wrong type. Instead of using ground broken pots, he advocated the use of fresh burnt raw clay, which, although requiring great care and some trouble in preparation, would be most efficacious.

Dr. Walter Rosenhain, D.Sc., F.R.S., then spoke, pointing out that the desiderata of a good refractory were—(1) non-fusibility, (2) resistance to chemical action, (3) facility of manufacture, (4) availability, (5) correct thermal coductivity. Unfortunately all these points could not be combined in one substance, and so no ideal refractory was on the market. Most glasses are "acid" fluxes and so liable to attack basic materials in the refractory. Thus it is that clays with increasing alumina content are so resistant to glasses. One great obstacle in the glass trade was the time taken in building and drying pots, and he hoped that in the near future pots would be made by a casting process. Regarding "grog" in pot building, he was of the opinion that slate could be used as a binding material and to alleviate shrinkage, giving as it would a sharp edged particle and also being very refractory. He also advocated the measuring of the plasticity of clay by means of the "penetrometer." Concluding his remarks, he spoke of the virtue of coating fireclay and potclay by specially refractory materials. In particular he mentioned the use of carborundum and of zirconia as being likely to yield results of a satisfactory nature.

Dr. P. C. H. Boswell spoke of the need of further investigation in the behaviour of potclays, and hoped that glass manufacturers themselves would experiment. In addition, little was known as yet as to the effect of small amounts of impurities in potclay. For example, might not titanium oxide have a deleterious effect? He discussed the purification of clay on a large scale, and also spoke of the future of surface combustion in glass manufacture.

Mr. Spiers, the Secretary of the Faraday Society, appealed to glass manufacturers to make known their difficulties regarding refractories. The main object of the Faraday Society was to concentrate on these difficulties, and up to the present they had had considerable success.

The July Meeting of the Society will be held on Wednesday, the 25th inst., in Manchester. Papers will be read on the "Action of Various Solvents upon Glass."

NOTICES OF BOOKS.

The Manufacture of Sulphuric Acid and Alkali. By George Lunge, Ph.D. Fourth Edition, Supplement to Vol. I. *Sulphuric and Nitric Acid.* London: Gurney and Jackson. 1917. Pp. xii+348. Price 15s. net.

In order to bring the text of the fourth edition of his treatise on sulphuric acid up to date Prof. Lunge has adopted the course of issuing a supplementary volume containing descriptions of new processes and of the work which has been done in the last few years, and by the use of the supplement together with the original volume readers can obtain the latest and fullest information on the manufacture of sulphuric acid and alkali. References to the fourth edition are given page by page, and an excellent index is provided dealing with the matter in the fourth edition as well as the supplement. It is no doubt needless to say that the greatest care has been taken in the preparation of this volume, which in every way maintains the high standard which is characteristic of Prof. Lunge's work.

Directory of Paper Makers of the United Kingdom for 1917. London: Marchant Singer and Co. Pp. 236. Price 1s. net.

In the 1917 edition of this directory the list of paper makers in the United Kingdom have been carefully revised, and many additions have been made to the list of water marks and trade names. A short account is given of the recognised customs of the paper trade as adopted by the Paper Makers' Association of Great Britain and Ireland, the Scottish Paper Makers' Association, and the Association of Wholesale Stationers, and the very numerous advertisements in the directory are well classified and indexed. Printers, stationers, publishers, and all users of paper will find the directory quite invaluable.

THE CHEMICAL NEWS

Vol. CXVI., No. 3007.

ELECTROLYTIC VALUATION OF IRON SULPHIDE.

By HOWELL WILLIAMS.

Iron sulphide is largely used in chemical works for removing second-group metals—chiefly arsenic—from commercial mineral acids. Its value naturally depends upon the amount of sulphur it contains in combination with iron as monosulphide, and which will be evolved as hydrogen sulphide on treatment with dilute mineral acid. Direct oxidation methods would be of no value, since by such methods the total sulphur present in the sample would be obtained.

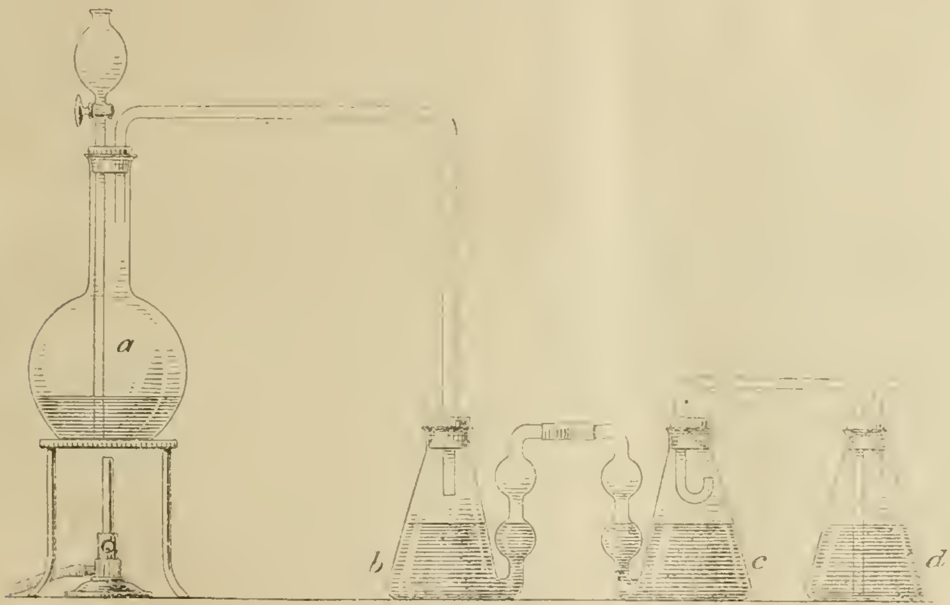
The method generally employed is that of absorption of the liberated hydrogen sulphide in sodium hydroxide solution and subsequent titration of the sodium sulphide produced by means of standard iodine solution. The results usually obtained by this method are low, perhaps due to the formation of complex sulphides when the concentration of sodium sulphide in the solution is high, and also due to the velocity of the reaction—

$$Na_2S+2HCl = 2NaCl+H_2S,$$

a little of the liberated hydrogen sulphide, thus escaping the iodine.

As a result of experiment I have found that sulphides can be most accurately determined by precipitating cadmium sulphide from a solution of a cadmium salt, and subsequently decomposing the metallic sulphide formed, and depositing the metal upon a weighed electrode.

The apparatus employed is that shown above. The Fresenius absorption flasks (*b* and *c*) are charged with 50 cc. each of a solution of cadmium chloride containing 100 grms. of $CdCl_2.2H_2O$ per litre of water and 5 cc. of concentrated hydrochloric acid. The Erlenmeyer flask (*d*) contains 25 cc. of the same solution.



(The tube in flask *c* should terminate in a fine point).

One gramme of the finely-divided sample is brushed into the 500 cc. evolution flask (*a*) together with 5 grms. of zinc, which must be free from sulphur. 100 cc. of dilute hydrochloric acid (sp. gr. 1·1) are introduced into the flask by means of a tap-funnel.

During the earlier part of the experiment the flask (*a*) should be cooled by placing in a basin containing cold water. As soon as evolution of gas slackens, the basin is removed and the flask is heated until the neck of the first absorption flask becomes hot.

The apparatus is then disconnected, and the contents of the absorption flasks are washed into a 500 cc. beaker. The cadmium sulphide is allowed to settle, the supernatant liquid is decanted through a 15 cm. filter, the precipitate washed a few times by decantation with warm water made just acidic with hydrochloric acid, and finally removed to the filter and washing continued until no precipitate is obtained by passing hydrogen sulphide through the washings.

The precipitate is removed to a small beaker with the aid of dilute hydrochloric acid and is boiled until solution of cadmium is complete. Precipitated sulphur is removed by filtration, and the filtrate collected in a 200 cc. electrolytic beaker.

The solution is neutralised with sodium hydroxide solution, using phenolphthalein as an indicator. A slight excess of sodium hydroxide is added and concentrated potassium cyanide solution until the cadmium hydroxide is just dissolved.

The solution is diluted to 120 cc. with water, and the solution is electrolysed with a current of 5 ampères and an E.M.F. of 5·5 volts, using a rotating cathode. When the deposition of the cadmium is complete, the cathode is washed with alcohol and dried at 100° C. The increase in weight of the cathode equals cadmium formerly combined as cadmium sulphide.

Weight of Cd × 0·2852 × 100 = per cent sulphur.
Per cent S × 2·74 = per cent iron sulphide.

Notes.

The addition of zinc to the evolution flask is made in order to maintain a reducing atmosphere and thus prevent the separation of sulphur; it also serves to dilute the gaseous mixture.

If the experiment is conducted carefully no precipitate is formed in the Erlenmeyer flask, in which case this solution may be ignored in subsequent operations. If, on the other hand, the quantity of precipitate is large, it is probable that absorption of hydrogen sulphide has been incomplete.

Great care must be exercised in washing the precipitated cadmium sulphide as it is slightly soluble in acidified warm water.

The time required to electrolyse the cadmium solution, using platinum gauze electrodes, is about one-and-a-half hours.

The results obtained in a series of experiments with this method were slightly low, but the maximum error obtained, using re-precipitated iron sulphide prepared from re-crystallised ferrous ammonium sulphate, did not exceed 0·5 per cent of the value theoretically required for iron monosulphide.

An attempt was made to use a solution of copper sulphate in place of cadmium chloride, but the results were invariably low, owing, no doubt, to the formation of a mixture of sulphides.

This method may also be applicable for the valuation of other sulphides.

SOME PRESENT NEEDS OF THE BRITISH RUBBER INDUSTRY.*

By WYNDHAM R. DUNSTAN, C.M.G., LL.D., F.R.S.,
Director of the Imperial Institute.

Last year the total export of British plantation rubber exceeded 70,000 tons, whilst the natural forests of Para trees in the Amazon district of Brazil exported only 34,629 tons. The Empire has already gained, and will certainly maintain, the premier position as the producer of the raw material, to the great benefit of the tropical countries of the Empire which furnish the commodity, contributing not merely to the prosperity of the planters, as individuals or companies, but to the general welfare of the countries concerned. Apart from the intrinsic value of the material for the manifold purposes of warfare, it may fairly be claimed that the generous contributions of the Governments of Ceylon and Malaya to the sinews of war, in money and material, are in no small measure the result of the prosperity of the rubber-planting industry.

Not less important than the production of the raw material is its utilisation within the Empire for industrial purposes. The Empire has command of the raw material, and it is desirable that so far as possible this material should be manufactured within it, manufactured goods and any surplus of the raw material not required for Imperial use being exported.

In this connection there is surely room for further enterprise and for co-operation between producer and manufacturer, both in this country and in the Dominions. In 1913 20,782 tons of British grown rubber were imported to the United States alone. In 1915 the United States took as much as 46,432 tons of British-grown rubber, or more than half the total export, whilst in addition nearly 20,000 tons was taken from Brazil. Apart from the special circumstances of war, which no doubt account in part for the increased export, it is evident that the United States has become the principal rubber manufacturing country of the world, deriving much of the rubber it uses from our Empire.

It may be added that some of the great rubber manufacturing enterprises in the United States have begun to acquire land in the tropics for rubber production, and this movement on the part of American manufacturers to secure a direct supply of the raw material under their own control has special significance. The problem for us is the reverse of theirs, and it will probably best be solved in the reverse manner.

This is not the occasion to discuss the economic factors, apart from the war, which have given the United States this pre-eminence in manufacture, but there is nothing discoverable which militates against the view that there is a need for futher enterprise in this country as well as in the Dominions, and especially in Canada, in the manufacturing industry. It is to the advantage of the Empire as a whole, especially in view of our increasing production of the raw material, that the rubber manufacturing industry should be increased and more trade created with foreign countries in the supply of manufactured rubber goods. Canada is not likely to wish, directly or indirectly, to depend in large part on the United States for the manufactured rubber goods she requires. Canada, as well as Australia, will no doubt desire to take a larger share in working up the raw material furnished by the tropical countries of the Empire. I refrain on this occasion from making more than brief allusion to this important aspect of the subject, which demands serious attention at the present juncture; but it may be suggested that those who produce rubber might co-operate with those who are in a position to manufacture it, to the great advantage of the entire British rubber industry. Some of the large profits which accrue from the production of rubber might well be applied to the extension of the rubber manufacturing industries here and elsewhere within the Empire.

I have been asked to make some reference to the assistance which the Imperial Institute has given to the rubber-growing industry, in supplying information and in conducting investigations into questions of fundamental importance.

From the inception of the British rubber-planting industry the Imperial Institute has rendered continuously scientific and technical assistance, both in information and research, to the Governments of every tropical country concerned in which planting has been attempted, and has published, especially in its "Bulletin," a very large amount of important information. In this connection mention may also be made of the article on "Rubber," contributed by the present writer to the last edition of the "Encyclopædia Britannica," and to the comprehensive volume in the Imperial Institute Series of "Handbooks to the Commercial Resources of the Tropics," entitled "Rubber: Its Sources, Cultivation, and Preparation," by Mr. Harold Brown, a member of the staff of the Scientific and Technical Department of the Imperial Institute, several other members of which have made important contributions in recent years to our knowledge of rubber.

Some of the earliest research work conducted at the Imperial Institute was a comprehensive study of the composition and properties of rubber from planted and wild trees, and it is interesting to recall now that one of its first reports was to the Government of India in 1900 on the quality of rubber obtained from Para rubber trees experimentally planted at Mergui, in Burma. In 1907 a further report on the quality of the Para rubber from Mergui showed it to be of excellent quality, comparing very favourably with plantation Para rubber from Ceylon and Malaya. Burma has been somewhat slow in its progress in this matter, and it still remains one of the several countries in which further developments in rubber planting, when such are called for, might well be undertaken.

A report presented to Parliament in 1912 shows that the Imperial Institute had conducted investigations on rubber and the various rubber-producing problems in connection with experimental production in the following countries of the Empire: India, Ceylon, Federated Malay States, Seychelles, Zanzibar, Uganda, East Africa, Sudan, Northern Nigeria, Southern Nigeria, Gold Coast, Sierra Leone, Gambia, Borneo, Sarawak, Natal, Transvaal, Zululand,

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* This article is reprinted from the Rubber Section of the Imperial and Foreign Trade Supplement of the *Times* December, 1916.

Rhodesia, and the West Indies. The sample rooms attached to the Scientific and Technical Department of the Institute contain a unique collection of authentic samples of rubber from all these countries which have been submitted to laboratory tests and valued for commercial purposes.

The rapid progress of rubber production in Ceylon and Malaya is too well known to need comment. In conjunction with the Agricultural Departments in those countries, the Imperial Institute has been identified with investigations of immediate practical importance. The same is true of other countries in which for one reason or another rubber planting has not been so successful in its results. There is one country, at present little heard of as a rubber producer, to which much attention has been given at the Imperial Institute, and after considerable investigation into more than one difficult problem success is at last apparent, and that is the portion of West Africa now known as the Southern Provinces of Nigeria, formerly Southern Nigeria. Here there is already one large plantation of about 1500 acres of Para rubber trees which has reached the producing stage, and the yield and quality of rubber from which is entirely satisfactory, and has recently been sold at the best prices in this country. Climate and soil in large tracts of the Southern Provinces of Nigeria are well suited to the growth of the Para tree, and native labour has proved to be suitable and adequate for the purpose.

There are few industries which open up a greater vista for enquiry and research than those of rubber production and rubber manufacture. In these two divisions of the great rubber industry there is a multitude of subjects of practical importance which demand systematic investigation. I can do no more now than allude in passing to some of these. They were considered in detail in my Address as President of the International Congress of Tropical Agriculture held in 1914 (*cf.* this "Bulletin," 1914, xii., 375), when important discussions took place on these subjects, in which planters and manufacturers and investigators from all parts of the world took part, and of which a full account is to be found in the "Proceedings" of this Congress, which were published in 1915.

In growing rubber trees in plantations problems arise as to the precise conditions most favourable to the life of the tree, to its growth, and to the maximum production of rubber. Closely connected with these problems are those of the effects of climate, soil, and manuring, and also of disease and insect attack and their remedies.

Equally important are the questions which arise as to the most effective times and methods of tapping the trees for latex, and there are others connected with the composition and coagulation of the latex and the best methods of preparing the raw rubber.

It is clear that most of these are questions which can only be investigated in the tropics. Much has been done in recent years to deal with these important matters, and it is right that full acknowledgment should be made of the valuable work which has been carried on in the tropics by and under the auspices of the superintendents and managers of estates in making exact observations and trials, in addition to the systematic investigations for which the Government Agricultural Departments have been responsible, and to the work conducted on a co-operative basis by the various planting companies represented in the Rubber Growers' Association.

The rubber planter, as a rule, has realised the precise importance of exact observation and experiment in the planting industry, and, in fact, he has recognised that he must be an accurate observer and investigator himself. A large amount of valuable research has been done, and is now in progress, and what is chiefly needed at the present time is co-ordination of results and more co-operation.

The allegation that Para rubber obtained from trees in plantations was inferior to rubber obtained from forest trees led, a few years ago, to the recognition of the importance of discussion and co-operation between the rubber-grower in the tropics and the manufacturer at home, so that the former may produce the substance that the latter requires. With this end in view a committee was formed at the Imperial Institute composed of representatives of the planting industry and of manufacturers in order to select the subjects of more immediate concern to the rubber industry as a whole which need elucidation by research. A plan of operations on these lines was drawn up necessitating experimental work in the tropics in connection with the latex, and experimental work in this country in connection with the raw rubber and its industrial employment. Arrangements were made for the work required in the tropics to be conducted in Ceylon with the assistance of the Government Agricultural Department and of some of the leading planting companies, and a joint committee was formed in Ceylon to be in communication with the committee in London. An extension of the Rubber Research Laboratory at the Imperial Institute provided for the special work required to be done in this country in co-operation with the manufacturers, who also placed their own laboratories and technical staff at the disposal of the committee. This scheme of work, conducted by competent investigators on both sides, has now been in full operation for over two years, and has been productive of results of importance both to the producer and the manufacturer, who have acted together on the committee both in formulating the plan of work and in selecting subjects for investigation, as well as in discussing the results obtained in relation to production and usage. The committee decided that whilst there should be the freest interchange of facts and opinions among those concerned, it was inexpedient to publish proposals for the modification of existing procedure in the production of rubber on estates until these had been thoroughly confirmed and substantiated by manufacturing tests.

The committee have now arrived at a number of important conclusions as a result of the researches conducted in Ceylon and at home, and these will shortly be published for general information. (The results of the examination of the first two series of samples of rubber are published in the present number of this "Bulletin" (pp. 495-566).

There can no longer be any doubt that plantation rubber, properly prepared, will equal, if not excel, for the purposes of manufacture, the rubber obtained from the forest trees of Brazil. There are, however, still a number of questions relating to the preparation of rubber in the tropics which require investigation in order to establish for general adoption a thoroughly satisfactory method of preparing rubber in the form best adapted for manufacturing use. In the course of the work which has been already done on this subject it is clear that research is also needed on the manufacturing side, in order to elucidate and improve methods which are at present largely empirical, and some of this investigation is being conducted by the principal rubber manufacturing companies in their own laboratories.

In order that effective progress may be made in research in connection with the rubber industry, the different spheres in which systematic research is required should be clearly recognised and provided for. There are matters requiring elucidation which are of immediate importance, both in production and in manufacture, and there are other and more fundamental questions in each of the two divisions which are the proper subjects of scientific research, and will take years of strictly scientific investigation to unravel. Research on the principal and urgent problems which now confront the rubber industry is best arranged and conducted by agreement and co-operation between those who are qualified to know what is required to be done and those who are qualified to do it. A modest beginning has been made on these lines at the Imperial Institute, through the committees to which I have referred, on which producers, manufacturers, and investigators are working together to solve certain selected problems which they agree it is of first importance to the industry should be attacked without delay, and to which they also agree the work should, to begin with, be limited. Work on these lines now needs extension.

There is, however, room for other work of a more general character, especially on the chemistry of the rubber molecule. Research of this general nature is, as a rule, best carried on in the research laboratories of universities and colleges, since it belongs in the first instance to the advancement of a particular science or sciences. From such discoveries the industrialist may ultimately greatly benefit.

There are some who hold the view that the whole of the research of both descriptions I have referred to, sometimes roughly classed as "practical" and "theoretical," required for the rubber producing and manufacturing industries should be centralised in one scheme and conducted at one institution. Any such scheme is, in my view, entirely impracticable and undesirable. The subject is too large and complicated in its various aspects to be dealt with in this way. There is room for research in the tropics and in all countries of the tropics, and there is room for work at home and in many places and directions at home. What is really important is that there should be a clear understanding and co-operation as to the problems to be solved, and a partition of the work in different places according to its requirements.

THE COLLOIDAL MEMBRANE: ITS PROPERTIES AND ITS FUNCTION IN THE OSMOTIC SYSTEM.*

By FRANK TINKER, D.Sc. (University of Birmingham).

During recent years the thermodynamic theory of osmosis has undergone considerable development at the hands of several mathematicians and physicists, who have shown that the osmotic pressure of a solution is a somewhat complex function of such diverse factors as the vapour pressures, specific volumes, coefficients of compressibility, heats of dilution, &c., of both the solution itself and of the pure solvent also. (See, for instance, the work of Porter, Trevor, G. N. Lewis, Bancroft, Van Laar, and others.) On the other hand, the kinetic side of the subject has remained more or less stationary, the majority of the theories purporting to explain the mechanism of osmosis having little to say with respect to how and why osmotic pressure is dependent on almost all the other physical properties of solutions. Inasmuch as the subject is evidently too complicated for *a priori* hypotheses, it seems desirable that we should study exhaustively all the parts which go to make up an osmotic system. More particularly, in addition to considering the properties of the pure solvent and solution themselves, we should include the membrane—its structure, properties, and behaviour to the solvent and solute respectively; and the conditions governing osmotic diffusion across it.

The common colloidal membranes of the copper-ferrocyanide type are built up by the aggregation of small colloidal particles ranging in diameter from 50 to 400 $\mu\mu$ (Tinker, *Proc. Roy. Soc.*, A, 1916, xcii., 357). The interstices between these particles form the pores of the membrane, the average capillary diameter being of the order of from 10 to 20 $\mu\mu$. Although the pore diameter is relatively great as compared with the diameter of the ordinary crystalloidal molecule, it is small enough for the whole of each capillary to be entirely under the influence of surface phenomena; and when osmotic flow takes place, say from a pure solvent to a solution, the moisture which diffuses is temporarily in the adsorbed or superficially condensed condition for such time as it is in contact with the membrane. Moreover, the adsorption effects shown by colloidal membranes are selective in nature; a copper-ferrocyanide film, for instance, taking up water rather than cane-sugar from aqueous solutions of the latter (Tinker, *Proc. Roy. Soc.*, A, 1917, contemporary number), thus explaining why this membrane is permeable to water but not to sugar. If the membrane is of a neutral nature, as is the case with the inner sheath of the skins inclosing barley seeds, its behaviour to the solute follows closely the lines laid down by the well-known Gibbs Thomson rule. The vegetable membrane just indicated adsorbs and is highly permeable to solutes such as the phenols, amines, and fatty acids, which gives solutions having a low surface tension; whilst, on the other hand, it is impermeable to the sugars, polyhydric alcohols, most inorganic salts, and other solutes whose solutions have high surface tensions (A. J. Brown and F. Tinker, *Proc. Roy. Soc.*, B., 1916, lxxxix., 373; the general osmotic properties of barley seeds have been discovered and studied by Prof. A. J. Brown). Evidently the property of selective permeability which such membranes possess is a direct consequence of the selective adsorption effects shown by the colloidal particles composing the membrane.

With regard to the cause for osmotic flow, the fact of fundamental importance is that a colloid usually absorbs more moisture from pure water than it does from an aqueous solution. Whereas, for example, 100 grms. dry colloidal copper-ferrocyanide imbibes about 30 grms. of moisture from pure water, the same amount of colloid takes up only 13 or 14 grms. of moisture from a 60 per cent sugar solution (Tinker, *Proc. Roy. Soc.*, A. contemporary number). An immediate deduction from this fact is that the side of a membrane in contact with a pure solvent has a greater moisture content than the side adjacent to a solution. Consequently diffusion of the solvent from one side of the membrane to the other takes place of necessity, owing to the impossibility of establishing equilibrium when the moisture content of the colloid is not uniform throughout. In other words, osmotic flow takes place because the pure solvent induces a greater pressure and concentration of moisture inside the membrane than the solution does. To prevent osmotic diffusion, a hydrostatic pressure must be applied to the solution. Provided the pressure is placed on the solution only and not on the membrane as well, the application of the pressure increases the amount of moisture taken up by that part of the colloid in contact with the solution; and when a hydrostatic pressure equal to the osmotic pressure is placed on the solution, the moisture pressure and concentration throughout the membrane becomes uniform, osmotic flow then ceasing. (Some unpublished work by Prof. A. J. Brown and myself indicates that if the pressure is placed on the membrane *as well as* on the solution, the amount of moisture taken up by the colloid does not increase.) In many respects osmotic diffusion is thus very similar in nature to the process of vapour distillation. As is well known, the vapour pressure and concentration is usually greater above the pure solvent than it is above the solution. Application of a hydrostatic pressure to a solution raises its vapour pressure, and when the applied pressure is equal to the osmotic pressure, the vapour pressures of the pure solvent and solution become equal to one another, the vapour distillation no longer proceeding in consequence (Sir J. J. Thomson, "Application of Dynamics," p. 171; A. W. Porter, *Proc. Roy. Soc.*, A, 1907, lxxix., 319). But although the two processes of osmotic flow and vapour distillation are essentially similar in character—both being diffusion phenomena—they are by no means identical. (A further important similarity is brought out when we consider the high temperature coefficient of the rate at which osmotic diffusion takes place—Earl of Berkeley and E. G. J. Hartley, *Proc. Roy. Soc.*, A, 1909, lxxxii., 271; it is highly probable that the rate of osmotic diffusion is an exponential function of the temperature having almost the same expontial constant as the ordinary vapour pressure-temperature curves). In particular, the moisture inside the pores of a membrane is in a very much more concentrated condition than it is inside the vapour phase proper, owing to the fact that it is condensed on the surfaces of the colloidal particles composing the membrane. In the case of water the membrane concentration would appear to be about 20,000 times as great as the concentration of water vapour proper.

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* Contribution to a General Discussion on "Osmotic Pressure" held by the Faraday Society May 1, 1917.

The analogy just indicated is, however, a very useful one. By means of it we can arrive at the reason for many of the anomalies met with in the phenomena of osmotic flow and osmotic pressure. The above justification of its use indicates that, for purposes of discussion and mathematical treatment, we can replace the actual membrane by a vacuum; except, of course, when considering those quantities, such as the *rate* of osmotic flow, whose magnitude is determined wholly or in part by the actual nature of the membrane—that is, we can regard a vacuum as a particular kind of membrane (impermeable. of course, to non-volatile solutes, but permeable to volatile ones), by the aid of which, on account of the relatively simple laws obeyed by vapours proper, we can arrive at the various factors governing the direction and power of osmotic flow, and the magnitude of the osmotic pressure which a particular solution can generate.

In this connection let us take first the case of osmotic flow between two solutions on which no external hydrostatic pressures are imposed. The direction of osmotic diffusion will be from the solution which generates the greater vapour pressure (*i.e.*, the greater *partial* vapour pressure of the solvent). Inasmuch as the vapour pressure of a solution depends partly on its concentration and partly on other factors, such as the volume change which the solvent undergoes during the process of dissolving the solute in it, the heat of dilution, the formation of hydrates in certain cases, &c., all these factors have a hand in determining the direction and power of osmotic flow. The main factor is usually the relative molecular concentrations of the two solutions; with the exception of heat of dilution, the effect on vapour pressure of the other factors is usually negligible; at least, this is so in the case of dilute and moderately strong solutions. If, however, we eliminate the concentration factor by working with two solutions having equal molecular strengths on opposite sides of the membrane, the direction of flow will be towards the solution which has the greater heat of dilution, since a positive heat of dilution tends to make the vapour pressure of a solution abnormally low. (If, of course, both solutions are ideal, having zero heats of dilution and equal surface tensions, &c., there will be no osmotic flow between them, provided that they are equally strong molecularly). In addition, since a solution which has a positive heat of dilution and abnormally low vapour pressure has also a high intrinsic pressure and surface tension, the direction of osmotic flow is likewise towards the solution which has the higher intrinsic pressure and surface tension. (F. P. Worley has written an excellent experimental paper on the relation between surface tension and vapour pressure—*Journ. Chem. Soc.*, 1914, i., p. 273. In this connection see also a paper by myself—*Phil. Mag.*, September, 1916). Herein comes the application of Traube's surface tension theory of osmosis. When limited as above to the case of osmotic flow between two solutions of approximately equal molecular strength, this theory is of considerable value in predicting under what conditions osmotic flow will be abnormal. It will be seen, however, that the surface tension theory only comes in when we are dealing with non-ideal solutions; nevertheless its scope of application would appear to be very extensive, since most actual solutions deviate from Raoult's law and are in consequence more or less non-ideal. (An ideal solution is one whose vapour pressure is given in terms of the vapour pressure of the pure solvent and its own concentration by Raoult's relation—$p' = \frac{N}{N+n}p$).

Consider next the factors determining the magnitude of the osmotic pressure of a solution. The central fact in this connection is the simultaneous increase of vapour pressure with the application of hydrostatic pressure. It is evident that we can define the osmotic pressure as the hydrostatic pressure which, when applied to the solution, raises the vapour pressure of the latter up to that of the pure solvent. Taking this definition as a basis, it is quite a simple matter to deduce directly the well-known formula connecting osmotic pressure with vapour pressure, without resorting to the somewhat cumbrous method of the thermodynamic cycle. (I gave such a deduction in the contemporary volume of the *Phil. Mag.*, May, 1917). It would appear also that, for dilute and moderately strong solutions at any rate, all the abnormalities in osmotic pressure owe their origin to abnormalities in vapour pressure. (The vapour pressure of a solution is abnormal when it deviates from Raoult's law; in the same way osmotic pressure is abnormal when it deviates from the value given by the expression for an ideal solution, viz.:—

$$P - \tfrac{1}{2}\beta p^2 = \frac{RT}{v}\log_e \frac{N+n}{N}$$

—*cf.* Findlay's "Osmotic Pressure," p. 31). Consequently many of the factors which tend to upset the simplicity of the laws of osmotic diffusion tend also to make osmotic pressures abnormal. In particular, it is clear that, if the vapour pressure of a solution under atmospheric pressure is abnormally low, its osmotic pressure will be abnormally high; the difference between its vapour pressure and that of the pure solvent, which has to be nullified by the application of a hydrostatic pressure to the solution before osmotic equilibrium can be attained, is greater than Raoult's law would require it to be. Consequently also the osmotic pressure is unduly high when the solution has a positive heat of dilution, or when it has a high intrinsic pressure and surface tension. (*Cf.* Bancroft, *Jour. Phys. Chem.*, 1906, x., 322).

The problem as to *why* the vapour pressure of a solution, and indirectly, therefore, the osmotic pressure also, should be related to its concentration, heat of dilution, surface tension, &c., is a much more fundamental and difficult one than the question just treated as to *how* these properties are related to one another. It will depend for its complete solution on the accumulation of much more knowledge appertaining to the liquid state than we possess at present. My personal opinion with regard to this question is that the change in vapour pressure which the process of solution entails is largely the result of simultaneous changes which are purely physical in nature. When a solute is added to a pure solvent, the internal or thermal pressure of the latter *inside* the liquid is generally diminished, on account of the increase in volume and "free space" which accompanies the addition of the solute. If the pressure of the solvent within the liquid phase is thus diminished by the process of solution, it will likewise be diminished in the vapour phase without the liquid. (I treat this problem more fully in a paper in the *Phil. Mag.*, September, 1916, p. 295; a complete analysis of the problem of the effect of these physical factors on vapour pressure and osmotic pressure will appear in a future number of the same magazine). On the other hand, it would appear that chemical effects such as the formation of hydrates or solvates only cause disturbances in the magnitude of the vapour pressure. Associated solvents perhaps excepted, it does not seem likely that such effects are pronounced enough to make them into the primary factors underlying these somewhat complicated phenomena of solution.

Royal Institution.—A General Meeting of the Members of the Royal Institution was held on the 2nd inst. The Duke of Northumberland, K.G., President, in the Chair. F. E. Robotham and R. D. Pullar were elected Members of the Royal Institution.

THE VALUE AND IMPORTANCE OF PHYSICAL EXERCISES FROM A NATIONAL STANDPOINT.*

By Major Sir WILLIAM MILLIGAN, M.D.

A nation's welfare depends upon the mental and physical efficiency of its citizens. The evolution of the human race has shown the importance of physical efficiency. Games and sports, valuable in their way, do not take the place of skilled instruction in physical exercises. It is one of the faults of our system of education not to sufficiently recognise the fact that mental development and bodily fitness are interdependent. If our universities would recognise physical training as an integral part of the undergraduate's curriculum the status of physical culture would be enhanced. In America the universities have done much for physical training and there are elaborate and successful arrangements in vogue at such universities as Harvard, Pennsylvania, &c., for the physical education of their undergraduates. Regular instruction in physical culture has been successfully carried out for years past in Germany, Scandinavia, Denmark, and other European countries.

The physical training in our public elementary schools gives excellent results, but unfortunately ceases too early in a child's life. Only a small proportion of boys and girls go on to the secondary schools, and the majority go out into the world too soon, from a physical point of view, in order to become wage earners. It should be made compulsory for every one to continue some standard system of physical training until, say, the age of 18. The time appears to have arrived when the Government, through a Ministry of Health, should have pressure brought to bear on it to face seriously the problem of the physical fitness of the people. With a falling birth rate, a heavy child mortality, and the havoc wrought among our young men as the result of the war, the country is in danger if efficient means are neglected to rear physically fit boys and girls, the future fathers and mothers of England.

That the tide of opinion is already turning may be judged from the recent deliberations of the Labour Party upon the programme of future education when *inter alia* certain resolutions were adopted *re* swimming baths, gymnasia, and the best known scheme of physical training, &c. The following suggestions were offered by the writer of the paper for discussion:—

(1) The establishment of a central anthropometric bureau for the recording of the height, weight, muscular development, &c., of the youth of the country, such general statistics being the best criterion of the physical degeneration or otherwise of the population.
(2) Compulsory drill for two hours a week in all primary and secondary schools, public schools, and universities.
(3) The provision by local authorities of open spaces and gymnasia for drilling purposes and games.
(4) The provision of competent instructors, male and female.

The provision of open spaces for drill is essential, and if the co-operation of the municipalities could be enlisted, and the right to drill in public parks granted, there seems no reason why systematic drilling on a large scale should not be begun at once. The statistics gathered by The Metropolitan Public Gardens Association show a very healthy and growing recognition of the value of open spaces in our large centres of population. Could we not induce our municipalities to ear-mark certain portions of the public parks and open spaces under their control as "Municipal training grounds," to which the children, the young adults, and young men and women up to the age of 18, could be sent for exercise and instruction under the supervision of municipal instructors responsible to the Local Education Committee.

By a process of devolution each county might be made responsible to a central authority in London for the physical education of its inhabitants, careful annual statistics being prepared by a central anthropometric bureau showing the physical development, height, weight, muscular strength, &c., of those subjected to whatever system of national training may in the future be adopted.

To our detriment we have no purely British system of physical culture—comparable to Swedish drill, German gymnastics, or American games—nothing, in fact, branded with national characteristics.

REPORT OF HIS MAJESTY'S INSPECTORS OF EXPLOSIVES FOR THE YEAR 1916.

To the Right Hon. the Secretary of State for the Home Department.

Sir,—In accordance with the 57th Section of the Explosives Act, 1875, we have the honour to submit the following Report on our proceedings during the year ending 31st December, 1916.

The work of the Department has again increased to a substantial extent, and it was deemed desirable in September last to appoint three additional Inspectors, namely, Major Sir James Douglas, Bart., late Royal Artillery, for some years Superintendent of the Royal Laboratory, Woolwich Arsenal, whose wide experience in the manufacture of ammunition has been of the greatest value; Mr. T. C. Taylor, and Mr. M. E. White, Inspectors under the Factory Acts, who, owing to their previous training in inspection work, have readily adapted themselves to their new duties.

Although nominally the inspection staff of the Department as existing at the commencement of the year was only doubled by these appointments, the benefit from the point of view of inspection is considerably more than this represents, inasmuch as owing to the continual changes going on, especially in factories producing material for the Trench Warfare Department of the Ministry of Munitions, it has been impossible to carry on the office work with only one Inspector as heretofore,

There has again been a large increase in the number of licensed factories, no less than 23 having been added during the year. As the same number of new factories were licensed in 1915, and two between August, 1914, and the end of that year, this gives a total of 48 factories added since the outbreak of war.

Since the additional Inspectors were not appointed until September, the full benefit of the increase of staff is not yet apparent, but it has enabled us to make 384 visits to factories and 600 visits to magazines, as compared with 207 and 464 respectively in 1915. We have also attended 35 inquests, and held 55 inquiries, as compared with 10 inquests and 23 inquiries during the previous year, and paid 121 miscellaneous visits, many of which were to factories under the control of the Ministry of Munitions, as compared with 55 similar visits in 1915.

The addition, however, of new factories represents but a small proportion of the actual increase of inspection work. All the important existing factories have been enormously increased in size, and the output from them duplicated several times over. The majority of the firework factories have been engaged in loading hand grenades, trench howitzer bombs, and other articles for the Trench Warfare Department. Almost daily some new proposition has been brought to our notice, and our advice sought on the best and safest methods of manufacture. Every department of the Ministry of Munitions, which is in any way connected with the production of explosives, including ammunition, has been in close touch with us, and we have reason to believe that our assistance has been appreciated.

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* Abstract of lecture delivered at the Royal Institute of Public Health, June 27, 1917.

Our position is a difficult one. Almost every question in regard to manufacture which is referred to us involves a conflict between safety and output for war purposes, and in many cases it has not been easy to reconcile these two factors. Every effort, however, has been made to do so, and although when modifying or amending the methods proposed to be employed in the manufacture of new devices and inventions, we have regarded the question of safety as of the first importance, we have in every instance given full consideration to that of output.

The general condition of the factories, having regard to the exceptional circumstances now obtaining, is highly satisfactory. We have considerable difficulty, however, in impressing on the picric acid manufacturers the necessity for strict observance of our requirements in regard to cleanliness and freedom from grit in danger buildings. These factories, as a rule, are offshoots of chemical factories which are of necessity difficult to keep clean, and this, no doubt, has a tendency to cause slackness on the part of employees when they are transferred to the picric acid works. Many cases of excessive quantities of picric acid being present in packing sheds have also come to our notice, and it has been a matter of much consideration whether it was our duty to institute proceedings in these cases. We decided, however, that as in almost every instance the congestion was due to causes outside the control of the manufacturer, and was mainly brought about by the enormous daily output, combined with the necessity for sampling by the Ministry of Munitions before removal, no useful object would be served by taking the matter into court.

In addition to the inspection work and the routine work of the office, a considerable amount of committee work has fallen to us during the year.

In March a committee was appointed by the Secretary of State to "Conduct such experiments as they consider necessary to test the value of dry powder fire extinguishers as compared with water and other first-aid fire appliances for extinguishing or effectively controlling fires such as are likely to be caused by bombs." The Chief Inspector served as chairman, and Major Crozier as a member of this committee. The general conclusion arrived at by the committee, after carrying out a series of interesting experiments, was that a plentiful supply of water is by far the best extinguishing agent, and that dry powder extinguishers are practically useless for extinguishing or effectively controlling fires likely to be caused by bombs. (*See* published Report, dated April 27, 1916. Cd. 8250. Price 1d.)

In September, Major Coningham was appointed by the Secretary of State as a Nautical Assessor at Formal Investigations, under Section 467 of the Merchant Shipping Act, 1894. He is also serving as a member of a committee appointed by the Minister of Munitions in connection with the storage of filled gun ammunition.

In November, owing to the occurrence in London of a serious accident at a filling station for cylinders of compressed acetylene gas, by which two persons were killed and several injured, the Secretary of State appointed a committee "to consider the existing regulations in regard to cylinders of dissolved acetylene compressed into a porous substance and to suggest amendments of these regulations where this appears desirable." On this committee, which is still engaged in carrying out the necessary experimental work, the Chief Inspector is serving as chairman and Major Crozier as member and secretary.

We continue to have the benefit of the skill and experience of Messrs. P. V. and F. H. Dupré as Chemical Advisers to the department. Owing to the cessation of importations and to the reduction in the number of new explosives submitted for authorisation, their work for the Department has again been considerably less than in normal times, but we are glad to state that the whole of their spare time is occupied in work for the Ministry of Munitions.

We give their report in full—

2, Edinburgh Mansions, Howick Place,
Westminster, S.W., 31st December, 1916.

Gentlemen,

The total number of samples examined during the year amounted to 306 only, about the same as in 1915.

The total number (53) of rejections is fairly normal, but the number (35) of rejections for faulty composition is somewhat high. This is, no doubt, partly due to the increased complexity of permitted explosives as a whole, but also, possibly, to some extent because, owing to war work, the manufacturers have not the time for quite such careful supervision of blasting explosives as before.

The use of nitrate of sodium in the place of nitrate of potassium still appears to be causing some difficulty in connection with the heat test, but not to such an extent as last year.

The number of new explosives examined (15) is the smallest for a good many years, and consequently the number of samples examined in connection with the Home Office Testing Station is also very low. This is, no doubt, owing to the more and more complete absorption of all energies in war work.

Although the amount of work done for the Home Office is so much below the normal, it has been impossible for us to carry out any research work, owing to the immense amount of time we have devoted to work for the Ministry of Munitions.

F. H. Dupré.
P. V. Dupré.

Accidents.—The total number of accidents with explosives reported to us during the year is 641, as compared with 485 for 1915. Of these, 363 occurred in manufacture, causing 195 deaths and injuries to 598 persons. The number of casualties is, unfortunately, very much higher than has ever been the case since the Explosives Act came into force, but it should be noted that no less than 144 deaths were due to two accidents, namely 106 in one accident on April 2, and 38 in another on August 21. Of the remaining 51, seven were killed at the Roburite Works on May 15, and seven at the Rainham Factory on September 14, and it is hardly too much to say that all these 158 fatalities might have been avoided if, instead of engaging in futile efforts to extinguish the fires, the factory officials concerned had cleared everyone away from the neighbourhood. Of the 363 accidents, 146 caused no loss of life or bodily injury, and of those injured a very large proportion received very trifling wounds.

Although, in view of the results for the previous year, when only 21 persons were killed in the manufacture of explosives, the present figures are disappointing, it is a matter of some satisfaction to have had brought to our notice many cases where serious accidents would more than probably have occurred if it had not been for the precautions we had required. Moreover, in comparing the figures with those of previous years, regard must be had not only to the vast increase in the number of persons employed in the manufacture of explosives and in the quantity of explosive produced, but also to the relative inexperience of many of those so employed and to the high pressure at which work is necessarily carried on.

Of special inquiries under Section 66, we have, during the past year, held 10, and reports on these were duly furnished; the reports, though necessarily confidential, have been communicated to those manufacturers who are concerned to act on the recommendations they contained.

The number of accidents under the heading of "Use and Miscellaneous" is 274, as compared with 276 in 1915. By these accidents, 45 persons were killed and 274 injured, as compared with 48 killed and 298 injured in the previous year. By far the larger number of these accidents occurred during blasting in mines and quarries, and there is nothing exceptional in the figures. In fact, having regard to the amount of unskilled labour now introduced into these places, it is somewhat surprising that accidents are not more numerous.

In connection with the conveyance of cordite paste from one factory to another, a proposal was made by those chiefly interested that, instead of being packed in wooden barrels, this material should be forwarded in packages, each consisting of a double bag, the outer one being of stout canvas, and the inner of a waterproof insertion material. The reasons given for this suggestion were, first, that barrels are now difficult to obtain, and, secondly, that after arrival at the factory, the barrels are the more dangerous to handle in contact with the very dusty explosive. The question was very carefully considered with special regard to the danger of freezing in cold weather, and it has been finally arranged that the vans in which this material is consigned by rail shall be steam-heated under conditions which will eliminate all danger from overheating, and this arrangement appears to give satisfaction.

Experiments.—In addition to the experiments already referred to as having been carried out in connection with the Committee on Fire Extinguishing Apparatus, the following took place in the course of the year—

In January, a test was made at the Factory of Perivale Explosives, Limited, to ascertain whether Triplex Safety Glass would be suitable as a screen to protect the operators when filling detonators. A block of triplex glass, 2½ ins. thick, was securely fixed by ½ in. angle-iron plates in a screen of timber 3 ins. thick, and 4500 grains weight of fulminate of mercury was fired close underneath the glass. The result was to shatter the wooden screen work, large pieces of timber flying 150 to 200 ft. in the air, but the triplex glass, although cracked in all directions, was found to be absolutely whole—a clear demonstration of the great protection to an operator that would be afforded by this glass during work with detonators.

On March 2, a further experiment to supplement that carried out at Messrs. Eley Brothers' works in 1915 was made to ascertain the effect of the explosion of a hopper containing various quantities of gunpowder on a floor of concrete or other substantial material with a view to establish a safe system of loading cartridges from hoppers situated above the ceiling of a loading room. A hopper of gunmetal, about $\frac{3}{10}$ of an inch thick, was fastened to a platform, representing a ceiling above a loading room, the joists being on edge 3 ins. apart, and measuring 9 ins. by 3 ins. On these rested an iron plate 4 ft. square and ⅜ in. thick, through the centre of which the supply pipe of the hopper was led. Above the iron plate the usual inch floor boards were placed, the whole of the joists, with wood blocks filling the intervals under the edges of the iron plate, being strongly bolted together. On firing 12 lbs. of fine-grain powder, the hopper was blown to pieces, and the floor boards on one side shifted, but the iron plate and timber joists were not affected in any way, an indication that, say, 10 lbs. of powder or small arm nitro-compound can safely be used under these conditions.

In May, at the suggestion of one of us, Lieut. E. W. Bovill, Bombing Officer, 11th Reserve Cavalry, carried out an experiment to ascertain whether the explosion of a hand grenade when packed for transport would communicate explosion to the other grenades in the box. The general result of the experiment was to show that, even when the 12 igniters were in the box with 12 grenades, the detonation of one grenade, although causing the detonation of all the igniters, did not communicate to the other grenades.

In November, Messrs. Dupré carried out some tests to ascertain whether the addition of 2 or 3 per cent of moisture to a fulminate composition would appreciably diminish its sensitiveness and render it safer for filling detonators than the dry composition. The results of their experiments indicated that the addition of as much as 5 per cent of moisture to a mixture of fulminate of mercury and chlorate of potassium gives no practical increase of safety either against explosion by shock or communication of the explosion of a portion of the mixture to the remainder, and that such mixtures should be treated with the same precautions as are usual when dealing with dry fulminate composition.

Miscellaneous.—The Testing Station at Rotherham has not been very busy during the year, only 11 explosives having been tested.

It is obvious that at the present time there is little opportunity for devising and introducing new Permitted Explosives for Coal Mines.

There have been 10 appeals under Section 10 of the Petroleum Act during the year, eight in connection with liquid petroleum and two with carbide of calcium. No accident of special interest with either of these materials has occurred, but two serious accidents have taken place owing to the explosion of cylinders of compressed acetylene. The first of these, to which reference has already been made, occurred on July 25 at the works of the A-L Meteorlite, Limited, at Wyndham Road, Camberwell, and was, in our opinion, almost certainly due to the bursting of a welded cylinder in consequence of a defective weld.

The second accident occurred at the works of Messrs. H. and C. Grayson, Limited, at Liverpool, where acetylene cylinders were used for welding. A defect weld was very probably the cause of this accident also, but it was alleged at the inquiry that the initial explosion was due to a pocket of gas in the porous substance which was exploded by a shock.

It is hoped that the Committee now sitting will be able to formulate regulations in regard to the traffic in these cylinders which will eliminate all danger in future.—We have the honour to be, Sir, your obedient Servants,

A. Cooper-Key, Major,
His Majesty's Chief Inspector of Explosives.
T. H. Crozier, Major,
H. Coningham, Major,
J. S. Douglas, Major,
Thos. C. Taylor,
M. E. White,
His Majesty's Inspectors of Explosives.

RECENT SUCCESSES OF AGRICULTURAL CO-OPERATION IN CANADA.*

The agricultural year 1915-1916 was exceptional in Canada in the three respects of high yield, the quality of the crops, and the high selling price of grain. These favourable conditions have allowed the three great co-operative organisations of the Western Provinces to develop their interior activity, to realise enormous profits, and consequently to gain an enormous amount of support in agricultural circles.

In the whole world there is nothing comparable to these three organisations—The Saskatchewan Co-operative Elevator Company, the Grain Growers' Grain Company in Manitoba, and the Alberta Farmers' Co-operative Elevator Company. They include at the present moment more than 48,000 shareholders; the total sum of their assets exceeds 8,000,000 dols., and their paid-up capital in shares is about 2,000,000 dols.

Last year 90,000,000 bushels of grain, or about a third of the total quantity produced in Canada for the market, passed through their hands. Their profits are represented by hundreds of thousands of dollars. The Manitoba Company realised last year a profit of 775,000 dols., the Saskatchewan Company one of 757,000 dols., the Alberta Company one of 282,000 dols. Their combined profits amounted, therefore, to 1,814,000 dols.

The three companies now own or work more than 500 local elevators. Including the buildings now in course of construction they dispose, or will do so shortly, of a storage capacity of more than 5,000,000 bushels.

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* From the *International Review of Agricultural Economics*, published by the International Institute of Agriculture, Rome, No. 3, March, 1917.

It is fair to note that the development of agricultural organisation in the Prairie provinces is largely due to the perseverance and the sane commercial and financial methods shown in the management of the Manitoba Grain Growers' Grain Company. These were the best means of advancing the cause of union and co-operation among the farmers.

It is also apposite to recall that these companies enjoy no special privileges. They compete with the purely commercial companies, and the tariffs they apply to the handling of grain are fixed either by the Canadian Grain Commission or by the Winnipeg Corn Exchange, which control them. Their activity and their success are, therefore, the more remarkable and are proof of the excellency of their methods.

The figures representing profits which we have given are far from affording an accurate idea of the advantages which farmers derive from this organisation. The departments for co-operative provision, which allow a farmer to procure the products and other foods he needs almost at cost price, without the intervention of middlemen, mean an enormous economy to farms. Wood, wire, coal, rope, agricultural machines and tools, are thus provided to their members by the companies in increasing quantities. The Manitoba Company has even bought vast extents of forest land in order to command the timber needed by its members, which it cuts down and markets itself. The sale of agricultural products other than grain by these companies is becoming increasingly important.

It is therefore not surprising that the report of the Manitoba Company concludes with a very promising forecast—

"If the shareholders and those whom they have placed in charge of the respective companies' business remain true to the principle and ideal which brought them into existence, they cannot fail to increase in the right direction their power and influence in the commercial life of Western Canada. While it is always dangerous to enter the realm of prophecy, it is not too much to expect that within the next ten years the farmers of Western Canada will be operating their own sawmills and their own flourmills, possibly their own coalmines and meat packing plants, and may be caring for their own fidelity and fire insurance."

The decision taken at the respective general meetings of the Manitoba Grain Growers' Grain Company and the Alberta Farmers' Co-operative Elevator Company to merge themselves into a single company which will be known as the "United Grain Growers" represents a fresh step towards the unification of agricultural organisation and co-operative action. The new combination will have a capital in shares of 5,000,000 dols. The eventual aim seems to be the concentration in one organisation of all the three great companies of Western Canada, but hitherto the Saskatchewan Company has not considered the question of merging itself in the other two.

MATERIALS AND MACHINES.

The Basis of Britannic Prosperity.

The B.E.P.O. Motive.

What is unique in the plan and purpose of the British Empire Producers' Organisation is its practical adaptation to the progressive industrial development of the Britannic Commonwealth for our own people and by our own people.

There are other associations and agencies devoted to the furtherance of Imperial Preference in fiscal policy; to the enlightenment of the public on the boundless wealth of our Empire and its intelligent husbandry; to the cultivation of a better mutual understanding between the scattered peoples of the Empire; to the improved sectional organisation of particular branches of industry.

The B.E.P.O. is with them, and is always ready and anxious to co-operate, while itself going further. For it is the only organisation which is actually engaged in the construction of a system of Empire trade communication and combination.

An Economic Commonwealth.

Forming our conception of a commonwealth of Britannic nations, each governing its own affairs, but perceiving its deep interest in the progressive welfare of the rest of the Empire, the first proposition towards mutual self-help is that British materials should be primarily developed for British manufactures. In other words, the proper customers for our boundless stores of metals are the engineering and allied industries in the United Kingdom and other Dominions. The proper customers for such materials, again, as rubber, sugar, cereals, copra, palm kernels, cotton, wool, jute, and many other riches of our Empire are the British factories and mills in which these products are refined or worked up for general consumption, or the British homes to which they are distributed direct.

Conversely, the proper customers for British machinery and other manufactures are the farming and planting and mining industries developing the vast national resources of an Empire which is still largely unexplored virgin territory.

The Path to Economic Freedom.

Necessary, therefore, as is the internal organisation of particular industries for common action and defence; valuable as may be conference between them and their allied or neighbouring associated industries, the B.E.P.O. claims that the most needed movement of all is the systematic linking together of the British and Overseas producers in practical schemes of mutual maintenance and development.

The people, for example, who have a business interest in the increase of British sugar growing are not merely the planters and the refiners and the makers of sugar machinery. They must embrace also the manufacturers of electrical apparatus to drive that machinery, and the shipping and rolling stock to distribute the product. We must go further and include the manufacturers of confectionery and other commodities who see now the importance of securing continuous supplies of cheap sugar by the encouragement of intensified production on British soil, instead of being dependent on the good graces of unfriendly neighbours. Finally, there is the community of housekeepers, still amazed and disgusted to find that they have been carelessly enjoying cheap sugar on sufferance from an enemy who had always cherished the hope of sooner or later reducing the British Isles by starvation.

A Self-Supporting Empire.

So with many other "natural products" and the machinery for their development and consumption. It is both good business and good politics to strive to make the Empire self-supporting, while able also to trade to mutual advantage with our Allies and with neutral countries in the surplus production of each state. And it is certainly not all sufficient that there should be preferential tariffs for the benefit of our Dominions and Allies. Permanent conference is also necessary between organised industrial interests. Machinery must be constructed for ready communication and practical co-operation between different industries and between different parts of the Empire. That is the work which has been undertaken by the B.E.P.O. with already great encouragement from powerful groups of manufacturers and other producers, as well as from the most enlightened statesmen of the United Kingdom and the British territories overseas.

T. [illegible]. E.

FEDERAL RESERVE BANKS IN THE UNITED STATES.*

Financial and banking organisation in the United States' certain defects of which were repeatedly pointed out by financial experts and economists and were thrown into relief by the crisis of 1907, has undergone in recent years a significant transformation.

Recurrent and multiplied attempts, and also numerous failures, profound study, and the resultant minute knowledge of the country's real needs and political necessities, seem at last to have led the Government of the States to institute a new organisation of banking, grafted on the surviving trading organisation and aiming at providing remedies for the crises which may eventually threaten the equilibrium of the money market.

The law of December 23, 1013, which created the Federal Reserve Banks, gives its bases to the new system and is modified and amplified by a law of September 7, 1916, which is connected at several points with the law on agricultural credit of July 17, 1916.

The new organisation represents, as we shall show in examining its outstanding features, a measured compromise between two political and economic principles—complete centralisation and localisation—which in turn have left their mark on the law and administration of the North American republic since first it was formed, and which the force of experience and of a union of social forces tend more and more to merge.

This question is the subject of an article, in which authorities are amply cited, in the April number of the *International Review of Agricultural Economics*, published by the International Institute of Agriculture at Rome.

The article first gives a general review of financial organisation in the United States. After two attempts to form a federal bank, Congress decided to care in future for its own funds, instituting, under the control of the administration, centres of deposit and sub-treasuries in the principal towns. This was the so-called system of sub-treasuries which was adopted in 1846 and is still in force, but has been amended to allow surplus funds to be deposited in the National Banks. In this period the number of "State" Banks, privileged to issue circulating notes, increased largely. The National are differentiated from the State banks because they may be founded in any territory of the Union and issue notes, secured by a pledge of United States stock, which are legal tender.

The lack of elasticity in the financial system, which rendered it unable to meet the crisis of 1907, caused Congress to decree that there should be a National Monetary Commission, charged to examine the financial and banking situation in all its aspects in the United States and in the principal European countries. This Commission favoured a greater centralisation of the banking system. It did not, however, propose the establishment of a single federal bank on the model of the great national banks of Europe, but the creation of a Reserve Association of America which would have the necessary authority and means to increase and reduce the volume of paper money in circulation as circumstances demanded. Congress, on December 23, 1913, voted the Act creating the Federal Reserve, in accordance with the principles and the hopes which the Commission had enunciated.

In accordance with this Act, the territory of the Union was divided into 12 districts, and it was decided that the banks should be at Boston, New York, Philadelphia, Cleveland, Richmond, Atlanta, Chicago, St. Louis, Minneapolis, Kansas City, Dallas, and San Francisco. Every National Bank is required to subscribe to the Federal Reserve Bank of the district in which it is situated 6 per cent of its own paid-up capital stock and surplus in gold or gold certificates. If the capital thus subscribed be insufficient, a certain amount of the stock may be allotted to the Government. No Federal Reserve bank may begin business with a subscribed capital less than 4,000,000 dols.

Each Federal Reserve bank is under the supervision and control of a board of nine directors, of whom three represent and are chosen by the stockholding banks, three must when elected be actively engaged in their district in commerce, agriculture, or other industrial pursuit, and three nominated by the Federal Reserve Board. The chairman of the board of directors is chosen by the Federal Reserve Board from the last named three, and also has the office of Federal Reserve Agent, acting as official representative of the Federal Reserve Board for the performance of the functions conferred on it by the Act.

The Federal Reserve Board which meets in Washington is the motive power of the whole system. It has seven members, namely the Secretary of the Treasury and the Comptroller of the Currency, who are members *ex officio*, and five others appointed to hold office for ten years by the President of the United States with the consent of the Senate. In appointing them the President has due regard to a fair representation of the different commercial, industrial, and geographical divisions of the country, and he designates one of them as governor and one as vice-governor of the Federal Reserve Board, the former being the board's active executive officer.

Previously National Banks were obliged to have a reserve equal to 25 per cent of the amount of their deposits in the reserve towns and 15 per cent in the other towns; but the Act of 1913 made this percentage 18 in New York, Chicago, and St. Louis, 15 in other reserve towns, and 12 in non-reserve towns. The excesses of available reserves should be transferred in accordance with certain conditions to the Federal Reserve Bank.

For twenty years from 1915 the member banks of a Federal Reserve Bank may apply to sell all or some of their circulating notes which they desire to retire. The Federal Reserve Board will decide on such applications. A Federal Reserve Bank may not purchase more than 25,000,000 dols. of such bonds in a year. Upon depositing with the Treasurer of the United States bonds so purchased, or any bonds with the circulating privilege acquired under this Act, any Federal Reserve Bank shall receive from the Comptroller of the Currency circulating notes in blank equal in amount to the par value of the deposited bonds. Such notes shall be issued and redeemed on the same terms and conditions as National Bank notes, except that they shall not be limited to the amount of the capital stock of the Federal Reserve Bank issuing them. Thus the circulation of notes will eventually be appreciably simplified and unified.

The law perfects the machinery for controlling the banks. In addition to the inspections by the Comptroller of the Currency, inspection of any bank by the Federal Reserve Bank of its district can be authorised by the Federal Reserve Board. The Federal Reserve Banks are themselves inspected annually and their member banks can obtain that they be inspected specially.

Both abroad and at home these banks are the Governments fiscal agents, and as such recover taxes and duties, pay arrears of the public debt, &c.

The Federal Reserve Banks were opened on November 16, 1914. Of the 7493 National Banks which were active only 18 refused their subscription. In June, 1916, the paid-up capital amounted to 54,864,000 dols. On June 17, 1916, they held United States bonds for 59,000,000 dols. Of municipal bonds, which are far less liquid, they then held 22,300,000 dols. Their foreign paper amounted to 64,953,000 dols.

On November 10, 1916, the liabilities of the Federal Banks amounted to 650,000,000 dols., represented as to one-tenth by the paid-up capital stock, and as to nine-tenths by the deposits of stockholding banks. Their own bills have hitherto circulated little, circumstances not rendering them necessaries. Their assets amounted to 400,000,000 dols. in gold, 110,000,000 dols. in paper, a certain quantity of their bills, and accounts with neighbouring banks.

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* From the *International Review of Agricultural Economics*, published by the International Institute of Agriculture, Rome, 8th year, No. 4, April, 1917.

The unification which the Federal Reserve system was designed to effect was shown first by the adoption of a method of weekly settlements of accounts among the various Federal Banks, the difference between the debit and credit sides of such accounts being rectified by a remitment of specie or bills. The displacement of assets from one district to another is thus reduced to the minimum. In the second place, since June 15, 1916, the recovery without charge of cheques and bills has been enforced by the Federal Reserve Board.

The Act of 1916 has enlarged the activity of the Federal Reserve Banks, notably in that it allows them to accept bills of exchange of home origin which are sufficiently guaranteed. It further allows the Federal Reserve Board to authorise "member banks to carry in the Federal Reserve Banks of their respective districts any portion of the reserves" previously required to be held in their own vaults; and in that it increases the facilities of member banks for short term credit, secured by bills not actually discounted. Any national banking association may apply to the Federal Reserve Board for permission "to establish branches in foreign countries or dependencies or insular possessions of the United States for the furtherance of the foreign commerce of the United States and to act if required to do so as fiscal agents of the United States."

Owing to the initial deposit of the reserves of member banks and the transfer allowed by this Act, the Federal Banks now hold about a quarter of the country's grand stock of gold.

Such is, in outline, the financial and banking system instituted in 1913 and revised in 1916. It is seen to have involved no radical upheaval of the previous organisation. It merely added some new wheels which centralised, and in some respects gave a new direction to, the complex and somewhat unequal mechanism constructed since the beginning of the Republic. The State Banks, the National Banks, the sub-treasuries, the circulation emanating from banks in direct contact with the people and secured by Federal Debt bonds, were not abolished. They subsist. But the concentration of a considerable part of the national gold reserves in a small number of Federal Banks, which could issue Federal notes in case of need, makes incontestably a regularising force in the money market, and will probably ensure the normal course of commercial and banking operations in times of crisis.

PROCEEDINGS OF SOCIETIES

CHEMICAL SOCIETY.

Ordinary Meeting, June 7, 1917.

Prof. W. J. Pope, M.A., D.Sc., F.R.S., President, in the Chair.

Messrs. S. Sugden, A. Fairbourne, and H. Merrick were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Tom Dempster, 7, Lugard Road, Aigburth, Liverpool; William Alexander Dickie, B Sc., 12a, Hythe Street, Dartford; Reginald Arthur Joyner, M.Sc., 38, Sidney Street, Saltcoats; Oscar Alfred Le Beau, B.A., B.Sc., 29, Rusthall Avenue, W. 4; Robert Ignatius Phipps, B.Sc., 36, York Street, Portman Square, W. 1; Arthur Stanley Quick, 123, Loughborough Park, S.W. 9.

The following papers were read:—

"The Constitution of Internal Diazo-oxides (Diazophenols)." (Part II.). By G. T. Morgan and H. P. Tomlins.

"The Phosphates of Calcium. Part IV. The Basic Phosphates." By H. Bassett, jun.

NOTICES OF BOOKS.

The Method of Enzyme Action. By James Beatty, M.A., M.D., D.P.H. London: J. and A. Churchill. Pp. ix+138. 1917. Price 5s. net.

This book has been written in the intervals of active service, in circumstances which, although they may, as the author suggests, have stimulated imagination and effort, made it impossible to refer to original papers. As such it must be regarded as a remarkable achievement, for it is a really important addition to the literature dealing with the nature and properties of enzymes, which workers in biochemistry cannot fail to appreciate. The theory of the mode of action of enzymes is admirably summarised in the preface by Prof. Starling. It is difficult in a very limited space to give any adequate details of the hypothesis. The author suggests that enzymes have a dual composition which is manifested in the power, common to all of them, of attracting the H or OH groups in water, and a specific power of adsorbing some particular substance. He hopes that other workers will be induced to continue the investigation of the enzymes, and to test his hypothesis as to the essential unity of the action of both the hydrolysing and oxidising enzymes and its reduction to the action of H and OH. The text is well arranged and is singularly clear and concise, and it is much to be hoped that work on the lines suggested by the author will be zealously taken up.

The Boy in Industry. With a Foreword by the Rt. Hon. Dr. Addison, M.P., the Minister of Munitions. Issued by the Ministry of Munitions under the authority of His Majesty's Stationery Office. Pp. 46. Price 3d.

This pamphlet contains three articles which appeared originally in the *Daily Telegraph* and which were certainly well worth reprinting in a more permanent and easily accessible form. The problem of boy labour is of the utmost importance to the industrial life of the nation, and it needs the most careful consideration and the fullest discussion at the present moment when unusual demands are being made upon boys under the age of 18, and exceptional opportunities are being given them. The articles contain some practical suggestions for the assistance of employers of labour and social workers, and questions of management, training, and supervision are discussed in an understanding and judicial spirit. Further information as to the suggested Welfare Scheme can be obtained from the Ministry of Munitions (Welfare Section), 6, Whitehall Gardens, London, S.W.

Memorandum on the Organisation of Scientific Research Institutions in the United States of America. By Gerald Lightfoot, M.A., F.S.S. Printed and Published for the Government of the Commonwealth of Australia by Albert J. Mullett, Government Printer for the State of Victoria.

This valuable report contains information which was collected as likely to be of interest in reference to the establishment in the Commonwealth of Australia of some permanent organisation for the promotion of scientific research and the application of science to industry. The work of national, State, and privately endowed institutions is described in some detail, and the general features of the organisation of some industrial laboratories are also discussed. Some of the conclusions that are drawn from the investigation are exceedingly interesting, and educational authorities in England will be able to learn a good deal from them. The desirability of divorcing research from instructional work, for instance, is considered with special reference to the experience gained at the Carnegie Institution, where it is regarded as largely a matter of temperament. The policy of making grants to students for the purpose of research is said to have ended mostly in failure. In the opinion of the authorities of the Rockefeller Institute the best teachers are those who are themselves doing research work, but the converse does not necessarily hold, and again it is regarded as mainly dependent upon individual temperament. The attitude of the Government of the United States towards scientific research is clearly shown in the memorandum, which is worthy of careful consideration by the authorities in England.

CORRESPONDENCE.

THE AERONAUTICAL INSTITUTE OF GREAT BRITAIN.

To the Editor of the Chemical News.

Sir,—There can be no longer any question that the result, or the duration, of the war depends to a considerable degree upon air power.

The supreme effort now being put forth by the Germans to get ready by next spring a gigantic air fleet, 3500 strong, manned by highly trained airmen, and with all necessary reserves of men and machines, has been made known by the recent official communiqué of the French Government.

The British and the French, together with our new Ally, the United States of America, are doubtless making an equally tremendous effort to meet this new move of the enemy. With our resources and those of our Allies there is little uncertainty of our being able to produce more warplanes than the Germans; but unless we can, on our side, also produce with equal rapidity a sufficient supply of highly-trained airmen, the numerical advantage given by the machines is naturally largely discounted.

General W. S. Brancker, until a few weeks ago, our Director of Air Organisation, in a paper on "The Training in Military Aviation," considered the question of the supply of trained airmen. In the course of it he said that one of the difficulties in dealing with the development of our air power was the question of the supply of airmen, because "the supply is for ever trying to catch up the demand, and the demand is for ever increasing both in numbers and quality."

This quotation from General Brancker's paper puts in a nutshell the difficulties as regards our supply of airmen. To help in this very important question of obtaining as many qualified airmen as rapidly as may be, the Institute has recently inaugurated special courses of instruction for young men about to apply for cadetships in the Air Service. Such preliminary training, if carried out on a sufficiently large scale, will enable the authorities to train our airmen much more rapidly than they could otherwise do.

The war work which the Institute has already started with regard to the preliminary training of our airmen, is invaluable. Extended without delay, on a generous scale, it must directly influence the immediate rate of development of our air power. In order to do this we have to find more motors, more wings, more aeroplane parts, more propellers, more aeronautical instruments, to increase our technical staff, and, incidentally, to procure more drawing tables and more accommodation generally.

Forced as it now finds itself either to limit the extent of this nationally urgent technical training to the means at its disposal, or to appeal for outside help, the Institute would fail in its duty if it did not make this need known; and, on patriotic grounds, it confidently asks you to help, either by becoming a member of the Institute or by giving it whatever financial assistance you can. At the same time we cordially invite you to come and satisfy yourself of the immediate utility and the practical nature of our undertaking.—Yours faithfully,

L. Blin Desbleds, Hon. Director.

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In a letter recently published in the *Times*, Commander C. B. Fry, who, as is well known, has had considerable experience in naval training at his training ship, T. S. *Mercury*, Southampton, endorsed the value of the Institute's work:—

"Sir,—Many young men under military age are, at the present time, keen to obtain preliminary qualifications likely to fit them for commissions in the Air Service. I should therefore like to call attention to the preliminary aeronautical course arranged by the Aeronautical Institute, of the Advisory Council of which I am a member. The course has been designed with great care to facilitate, and possibly accelerate, the training of our air officers.—Yours faithfully, (Signed) C. B. Fry, Commander, R.N.R."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 18, April 30, 1917.

This number contains no chemical matter.

No. 19, May 7, 1917.

Fluorides of Zirconium and Fluorides of Zirconyl. —Ed. Chauvenet.—The author has prepared zirconium fluoride by heating the acid fluoride of zirconyl (either anhydrous or hydrated) to about 200° in an atmosphere of hydrofluoric acid. The acid fluoride can be obtained by evaporating a solution of zirconia hydrate in hydrofluoric acid until crystals begin to appear. When dried to constant weight the compound has the composition $ZrF_4.3H_2O$. From the study of the compounds of zirconium it is found that on the one hand the compounds of this element have a very marked tendency to hydrolyse, while on the other hand the hydrated compounds must be regarded, not as derivatives of zirconium, but as derivatives of the zirconyl radical ZnO; the existence of this radical has been proved by determinations of electric conductivity and by cryoscopic and thermo-chemical measurements. The reactions which give rise to zirconium fluoride are $ZrOF_2.2HF = ZrF_4 + H_2O$; $ZrOF_2.2HF.2H_2O = ZrF_4 + 3H_2O$. The product is insoluble in water; it absorbs hydrofluoric acid in the cold, giving probably ZrF_6H_2. $ZrOF_2.2HF.2H_2O$ is stable in dry air, and even in vacuo at the ordinary temperature. It begins to lose water at 100° and at 140° it loses two molecules of water giving $ZrOF_2.2HF$. Above 140° and in air the acid fluoride of zirconyl gives up two molecules of HF, the residue being the neutral fluoride of zirconyl $ZrOF_2$. In the cold this compound absorbs HF and the acid fluoride is regenerated. The acid hydrated fluoride is soluble in water, but if the solution is diluted a product is deposited which, when dried to constant weight, possesses the formula $ZrOF.2HH_2O$. At 100° it loses 1·5 molecules of water, and at 120° the dehydration is total, the anhydrous neutral fluoride of zirconyl $ZrOF_2$ being obtained.

THE CHEMICAL NEWS

VOL. CXVI., No. 3008.

SOME ENQUIRIES INTO THE EXPLANATION OF RADIUM DISINTEGRATION.

By TARINI CHARAN CHOUDHARI, M.A.,
Government of Bengal Research Scholar.

Introduction.

RADIUM salts as well as radium itself give out emanations of which, up to the present, four distinct constituent rays have been recognised—the α, β, γ, and δ rays; the α-rays being material particles with positive electrical charge, and supposed by Dr. Rutherford to consist of helium atoms; β-rays being negative electrical and non-material in character (Kaufmann, *Phys.-Zeit.*, 1912, iv., 54), ejecting with great velocity approaching that of light; while γ-rays are regarded as ether pulsations, identified with Röntgen rays; they are supposed to be produced by the bombardment of the β-rays inside the solid radium salt; or if the salt is in solution, inside the radium atom. The δ-rays have not been much studied.

It has been found that the disruption of the radium molecule is accompanied by a relatively enormous evolution of heat. Rutherford has found that of this heat 75 per cent is derived from the emanation and its subsequent products of change. The Curies found that 1 grm. of radium evolves no less than 100 cals. per hour; hence 1·3 cubic millimetres, the amount of emanation yielded per hour by 1 grm. of radium, must be responsible for 75 cals. Comparing this with the heat evolved by a violent chamical change of the ordinary character, the difference is enormous. From mathematical considerations it has been found that the amount of energy parted with during the disruption of an atom is hardly commensurable with that due to its combination with another atom to form a compound. (Ramsay's "Gases of the Atmosphere," p. 290).

Now the disintegration of radium goes on in the solid state as well as in the solution of its salt, generally the bromide being used in investigations. The present communication is mainly concerned with the disintegration of radium halide in aqueous solution, and also to some extent with disintegration in the solid condition of the salt.

Points which present Anomalies.

The writer wishes to discuss briefly the following points:—

(1). It has been found that the gases evolved from a solution of radium bromide consist of a mixture of hydrogen and oxygen in nearly the proportion of two to one, with a small excess of hydrogen (to the amount of about 6 per cent of the total gas), the emanation being mixed with these gases. How is this excess of hydrogen to be satisfactorily explained?

(2). As during the process of disintegration radium bromide (in aqueous solution or in solid state) continually gives out emanation which, among others, contains material particles, the mass of radium in the salt progressively diminishes, and in fact, the salt continually decreases in weight. How is this decrease in weight of radium bromide to be *fully* accounted for?

(3). As atomic disintegration proceeds, it is the weight of metallic radium present in any known weight of radium bromide that undergoes diminution in weight; and the halogen part has nothing to do with the process of disintegration of its metallic partner; and as the process goes on, the amount of metallic radium in combination with bromine continually diminishes and finally completely disintegrates. But what becomes of the equivalent quantity of bromine originally combined with radium in the bromide?

Discussions and Considerations.

The above points will be taken up in the order stated.

(i.) Aqueous solution of radium bromide, as is well known, gives a mixture of hydrogen and oxygen together with emanation, the hydrogen being always found in a larger proportion than two to one. Hydrogen and oxygen certainly come from the decomposition of water; but why are they not found in the proportion of 2 to 1? "The gases evolved in eight days from 60 milligrms. of radium bromide in aqueous solution were exploded in a small explosion-burette; the residual hydrogen was left . . . containing emanation" (*loc. cit.*, 286). Various causes have been suggested to explain the excess of hydrogen in the decomposition of water by radium, one of which, as previously advanced, that this is due to oxidation of grease of stopcocks used in the experiments, has been disproved. Ramsay was unable to detect any formation of ozone; he also holds that no hydrogen peroxide or radium bromate is produced, as he could not chemically detect the presence of any of them, possibly owing to the microscopic quantity of bromide itself (Ramsay, *Meddel. K.-Vet. Akad. Nobelinst.*, 1905, i., 909).

The view that hydrogen is found in excess probably because part of the oxygen in the nascent state goes to oxidise radium bromide in solution to radium bromate, $Rd(BrO_3)_2$, thereby causing a relative diminution in the volume of oxygen, is not, however, feasible on theoretical grounds alone. If any bromate is formed at all in solution, the position of $2BrO_3$-ion becomes very insecure As will be explained later on, the 2Br-ion, produced from the electrolytic dissociation of $RdBr_2$, seems to be without any *locus standi* as disintegration proceeds; and therefore the position of $2BrO_3$, if any bromate is formed at all, cannot be more safe.

Ramsay, although, repeatedly states (*loc. cit.*) that it does not appear possible that hydrogen is produced from emanation—a case of transmutation—seems, however, tacitly to tend to that view, proving the absence of other alternatives by somewhat of the method of "proof by exhaustion."

It is difficult to subscribe to his view; and the reliability of chemical tests alone which have hitherto failed to detect the extremely microscopic quantities of products is difficult to accept as convincing.

Taking into consideration that the excess of hydrogen is small, only 6 per cent, the deficit in oxygen, although very small, may not be due to any *one* cause. It is probable that, in the presence of emanation, part of oxygen which is produced from the decomposition of water may be oxidised to ozone, and a part may go to oxidise water into hydrogen peroxide, and hydrogen remaining relatively in excess.

(ii.) As this (process of disintegration) goes on, the radium (bromide)—see Note—will continually decrease in weight. To what is this diminution in weight actually due? Radium bromide being isomorphous with the corresponding barium halide, it has the formula RdB_2. As disintegration proceeds, the weight of metallic radium present in any given weight of the bromide gradually diminishes, owing as is well known to the escape of material α-particles, causing thereby a progressive diminution in the salt as a whole.

(NOTE.—Metallic radium was discovered by Curie and Debierne only in 1910. In the language of radio-activity, the word radium implies generally its salts and not the metal itself. As the negative radical in combination with metallic radium has absolutely nothing to do with the disintegration phenomena, in speaking of the "disintegration of radium" the word "metallic" or "atomic" should, for the sake of convenience and accuracy, be prefixed to the word "radium").

Now it appears questionable that as disruption of radium takes place, what becomes of its fellow, the quantity o bromine equivalent to the weight of radium which dis integrates; and, finally, when the total weight of metalli radium has disintegrated, what then becomes of the equivalent quantity of bromine which must have been set free from radium? Bromine has certainly nothing to do with the disintegration phenomena apart from the fact that it may have "induced activity" in the presence of emanation. I may here profitably quote the description of an experiment given by Prof. Ramsay, a part of which has already been quoted before. "The gases evolved in eight days from 60 milligrms. of radium bromide in aqueous solution were exploded by a spark in a small explosion burette; *the residue of hydrogen was left in contact with moist caustic potash* for some time. . . . The residual hydrogen, containing emanation, passed through a tube containing phosphorus pentoxide, &c." (Sir W. Ramsay's "Gases of the Atmosphere," p. 286.)

Nowhere is any mention whatever found of the disengaged helpless halogen; it appears that the bromine was probably absorbed by the moist caustic potash; taking for granted that no unforeseen or unexpected phenomenon, for example, combination between bromine and oxygen—a compound of which is hitherto unknown—takes place in the presence of emanation (which affects even glass and oxygen, and oxidises mercury) when mixture was sparked in the presence of the *emanations* (Makower and Geiger, "Practical Measurements in Radio-activity," p. 129).

From the above considerations it is clear that the diminution in the weight of radium salt at any particular moment is due to disintegration, as hitherto *explicitly* stated, only *partially* explains the position. The progressive diminution in the weight of the radium halide is evidently due to the joint effect of the amount of metallic radium disintegrated and to its equivalent weight of halogen set free from the salt owing to the disappearance of a corresponding weight of radium partner by disintegration.

(iii.) On gradual and finally on complete disintegration of the radium content of a salt what becomes of the bromine which was in combination with it originally? It has been already suggested before, according to the nature of the experiment described there, that it might have been absorbed by moist caustic potash; but caustic potash does not appear to have been used in every experiment, nor is there any mention of any other absorbent of halogen in lieu of potash.

Again, it appears that when disintegration takes place in an aqueous solution of the halide, the liberated halogen may remain dissolved in the water; but still a small fraction of it is likely to be in the gaseous state. Moreover, as has been mentioned before, enormous heat is liberated during radium disintegration; so long as the source of that heat, namely radium and emanation, remains it seems unlikely that the total quantity of volatile halogen should remain dissolved. What appears probable is that some chlorine or bromine may be mixed with hydrogen, oxygen, and emanations when a solution of radium bromide is considered, or the gaseous halogen may be with emanation, alone, when the disintegration takes place in the solid state. But at any rate, the halogen cannot be in combination with any of the near or remote disintegration products; for, the emanation (niton) and immediate products therefrom are of a non-metallic and inert character; and also for the fact that the remote products of change, for instance, radium D and radium F, are found to be of elementary nature from a study of their spectra.

One passage must be quoted for clearness of position. "If a radium solution is kept for some time in a closed flask, the emanation steadily accumulates with time; half of the equilibrium amount forming in four days, three quarters in eight days, and so on, equilibrium being practically reached in three or four weeks. *In addition, hydrogen and oxygen* are formed from the solution by the radio-active decomposition of water. On exploding the gases, a slight excess of hydrogen remains with the emanation. This may be admitted in a vacuous bulb immersed in liquid air. The emanation is condensed; and the hydrogen, together with any helium produced from the emanation, can be pumped away" (F. Soddy's "Chemistry of the Radio Elements," pp. 52—53). Thus here is also absolutely no reference of any halogen being mixed up with emanation or the condensed emanation. The liquid emanation itself is described by Ramsay and Gray as colourless and transparent (Gray and Ramsay, *Trans.*, 1909, xcv., 1073); so there is apparently no chance of halogen admixture. (The following sources and authorities have been consulted on the subject, in addition to what has been referred to:—Dr. Rutherford's "Radio-activity," H. C. Jones' "The Electrical Nature of Matter and Radio-activity," 1911, and Dr. Rutherford's "Radio-active Transformations"—Silliman Lecture Series, 1912). The *radium emanation* from radium bromide in water which also yields "electrolytic gases," containing an excess of hydrogen, was collected. *The gas was exploded*, and the residual hydrogen and radium emanation dried, transferred to a small glass vessel and condensed by cooling in liquid air. . . . Hydrogen was removed by a mercury pump until the escaping gases were slightly luminous, due to the appreciable vapour pressure of the radium emanation at the temperature of the liquid air. After the *removal of hydrogen* the emanation was rendered gaseous. . . . The volume of radium emanation gradually diminished and the luminosity faded, until at the end of a month all luminosity had disappeared; on gently warming the tube a quantity of gas, four times the volume of the original emanation, was obtained; and this gas gave the *helium spectrum*. The spectroscopic studies have been made of these products (Sir W. Ramsay, *Comptes Rendus*, 1904, cxxxviii., 1388—1391); but no reference to bromine-removal or its spectrum mixed with the other products of radium-change is referred to.

Ramsay and Collie have carefully studied the spectrum of the emanation from radium bromide which has been mapped with as great exactness as possible, and the observed lines are recorded in their paper (*Proc. Roy. Soc.*, 1904, lxxiii., 470—476). Great confusion, however, arises inasmuch as, although the spectrum of the emanation is very brilliant at first, it is in a few minutes completely marked by hydrogen spectrum. As to the origin of this hydrogen there is a great controversy and speculation. The same authors suggest (*loc. cit.*) that it may have come from the electrodes; the emanation may not have been completely dried or hydrogen as well, like halogen, may be one of the disintegration products. No reference to Br spectrum is to be found herein.

It is impossible not to mention a high authority on the subject of radio activity, for we miss the mention of the point in his most accurate experimental details (Rutherford, *Phil. Mag.*, 1908, xvi., 300). No mention also is found in the nice small book on "Practical Measurement in Radio-activity," by Makower and Geiger (Manchester). In describing the "separation of emanation from radium solutions" the authors say in one place:—

"To further purify the emanation the gases remaining are exposed for some hours to caustic potash, which removes carbon dioxide and water vapour. To carry out the process, a *small glass tube is coated with a thin film of potash, obtained by pressing a small piece of potash in the tube, melting it by gentle warming*" (*Ibid.*, pp. 129—30). It is evident that the thin film from *a small piece of fused potash* cannot possibly be a perfect absorbent for Br in the presence of CO_2 and H_2O, which will be more greedily absorbed, and if Br actually forms a potash salt its presence has not been detected there. It may be possible that Br, partly at least, may pass even with emanation during pumping, and should give its characteristic spectrum with the emanation or disfigure the spectrum of the products from radium disintegration. It should be pointed out, however, that Ramsay in his paper exclusively on the instability or disintegration of $RdBr_2$ (*Monatsh.*, 1908, xxix., 1013) does not deal with these points. No investigator is found to make any mention of the halogen being mixed with hydrogen, oxygen, and emanation, or with emanation alone, as the case may be.

It would be evident from the foregoing arguments that the points deserve clear and definite exposition. As radium is an enormously costly substance, and is still a chemical curiosity, it is not possible to undertake an investigation on the subject in a laboratory unless specially equipped for the purpose; nor is it possible that the subject be skilfully handled by any ordinary experimenter when the products can hardly be identified by refined chemical means. The attention of the worker or thinkers on radium is invited to the fate of its unfortunate partner, with which it may be in chemical union.

It should be clearly stated, however, that radium-A, radium-B, radium-C, radium-D, radium-E and E_2, and radium-F *are all produced from emanation*, resulting from radium, by degradation. With this emanation the halogen cannot be in combination, as it is found to be chemically inert and of elementary nature; nor is it mixed with the emanation, as the spectroscopic examination does not bear that out (Ramsay and Collie, *Proc. Roy. Soc.*, 1904, lxxiii., 470).

Summary.

The points discussed and suggested in the present communication are that:—

(1). During the disintegration of a radium halide in aqueous solution, the excess of hydrogen cannot be satisfactorily explained by any *one* cause, and may perhaps be due to the consumption of oxygen, partly by ozonisation and partly by peroxide formation.

(2). When radium halide disintegrates the gradual diminution in weight cannot be attributed to the gradual disruption of its radium content alone, but is due to the quantity of metallic radium disintegrated, plus its equivalent quantity of halogen set free.

(3). The fate of the halogen content in radium halide when metallic radium has completely disintegrated, giving rise to emanation, remains *unexplained.*

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COLLOIDS.*

By F. DANVERS POWER.

Between the years 1861 and 1864 Thomas Graham published several papers giving the results of his discoveries in connection with dialyses. He found that when certain dissolved substances were separated from a surrounding solvent by an organic membrane, such as parchment, fish bladder, or collodion, some of them passed through the membrane freely into the surrounding solvent, while others remained behind, or only diffused very slowly. As a rule those substances that passed through were known to crystallise, so were given the name of Crystalloids, while those that remained behind were amorphous, like glue, gelatine, &c., and were called Colloids. The process of diffusion through membranes is termed Osmose. The reason for this phenomenon is evidently because the particles or aggregates of the colloid are too large to pass through the pores in the membrane. Graham further discovered that a number of substances generally considered as insoluble could be obtained in what at first appeared to be real solutions, *i.e.*, they were perfectly clear and seemingly homogeneous, but they did not diffuse through parchment. Graham called them Colloidal Solutions, or Sols, for short. Other substances besides water are capable of forming colloidal solutions, *e.g.*, alcohol, glycerine, organic substances, &c., and these are known as hydrosols, alcosols, glycerosols, organosols, &c. Sols are further distinguished from a true solution (such as a solution of sulphate of copper in water) by the addition of very small quantities of electrolytes, such as do not react at all with the dissolved substances, causing a radical alteration in the condition of the solution; for instance, a trace of carbon dioxide added to a sililic acid sol causes it to set to a translucent jelly. The products obtained by the coagulation of sols are known as Gels, and these gels have a capacity for taking dissolved substances out of solution and retaining them, which phenomenon is known as Adsorption. If a single compound is dissolved in a dissociating solvent, the ions may not be adsorbed equally, so the solution, originally neutral, may, after adsorption, become acid or alkaline.

There are various ways by which chemists may decompose compounds into simpler compounds, or into their elements, such as by heat, electricity, chemical affinity, light, pressure, and concussion. Decomposition by means of the electric current is termed Electrolysis, and the compound which is thus decomposed is termed an electrolyte. The electrolyte must be in a liquid condition, either in solution or in a fused state. The current from a voltaic battery, when passed through the electrolyte, decomposes it into two constituents known as Ions. Electrolytes must be compounds, and conductors of the electric currrnt. These compounds generally consist of a conductor and a non-conductor of electricity. The constituents of the electrolyte into which it is resolved are eliminated at the opposing surfaces of the two electrodes and never in the intervening liquid. Those that evolve at the negative electrode are known as electropositive, and include hydrogen, the alkalies, and metals; while those appearing at the positive electrode, such as oxygen, chlorine, bromine, iodine, and acids, are called electro-negative.

Colloidal solutions consist of at least two varieties of matter: (*a*) a liquid, and (*b*) a finely-divided solid or liquid substance in the former. These components of the solution are known as Phases. The colloidally dissolved substance is known as the Disperse Phase, and the solvent as the Continuous Phase. Dispersoids are classified into: (*a*) Proper or coarse dispersions (suspensions, emulsions, &c.), (*b*) Colloidal solutions, (*c*) Molecular dispersoids, and (*d*) Ionic dispersoids.

For the sake of convenience an arbitrary limit has been placed to the size of solid particles. Suspensions are particles over 0·1 micron in mean diameter, a micron being one-thousandth of a millimetre. Colloidal solutions, particles between 0·1 and 0·001 micron in mean diameter, and true solutions, particles under 0·001 micron in mean diameter.

All sols which appear clear to the eye and many which appear turbid, fail to show any particles through the microscope with ordinary methods of illumination, the reason being that the particles are small in comparison with the wave-length of light, and so are invisible. When a particle cannot be distinguished by an ordinary microscope, it is said to be "ultramicroscopic." The ultramicroscope invented in 1915 by R. Zsigmondy and H. Siedentopf, has demonstrated conclusively that colloids as Graham understood them are not a definite form, but a state of matter, and that by suitable methods a large number of substances can be prepared in a colloidal state that also occur in a crystalline condition. Sodium chloride, which is a crystalline substance, has been prepared as a colloidal solution in petroleum ether. Most of the metals have been obtained as sols, even the alkali metals, also a large number of sols of oxides, hydroxides, and sulphides are known.

Solid particles of microscopic size distributed through a liquid are called suspensions, while those solutions having two liquid phases are called emulsions. The dissolved substance in a colloidal solution may be separated in an insoluble form or gel by mechanical means or by heating. On increasing the concentration by heat or by adding small quantities of certain bodies such as electrolytes, they are transferred into jellies, or in dilute solutions precipitated, generally in an insoluble condition. The process of gel formation is variously known as coagulation, flocculation, or precipitation. Suspensoid sols are unstable in the presence of electrolytes. The first step in the coagulation of suspensoids is to neutralise their electric charges, which is done by the oppositely charged ions of the electrolyte. On adding the electrolyte to the sol, the particles are dis-

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* From the *Mining Engineer*, Sydney.

A Classification of Colloids.

Solid medium.	Liquid medium.	Gaseous medium.
Solid particle—		
Many cryptocrystalline ores, especially those containing finely-divided metals. Most solidified slags. Glazes, glasses, &c.	Ordinary suspensions and colloidal solutions of solid particles. Slimes, thickened or not. Wet plastic clays, &c. Turbidity in water. Deflocculated graphite, &c.	Fume and smoke. Flue dust. Dust of mines, flour mills, factories, &c. Systems involved in processes of air separation &c.
Liquid particle—		
Liquid inclusions in crystals. Much occluded water and water of crystallisation. Some filter cakes, &c., while wet.	Emulsions. Oil in condenser water and water in fuel oil. Oil flotation systems. The glue-like organic colloids.	Fog, cloud, and wet steam. Acid fume, collection of acid from smelters, fertiliser works, &c. Oil sprays, oil burners, &c.
Gaseous particle—		
Dry filter cakes. Silica brick and many other refractories. Mineral wool and metal sponge. Gas inclusions in crystals.	Foams and froths. Wet steam (phenomena of foaming in boilers). Systems used in gas and foam processes of ore separation.	No tangible examples.

charged, as they no longer repel one another, they are free to approach and form large aggregates which settle.

Hydrosols may be reversible or irreversible, according to whether the dried residue is soluble or insoluble in the solvent employed. The formation of reversible gels is accompanied by a change in the distribution of water. To take homely instances—gelatine when heated above a certain temperature, depending on its concentration, forms a solution, and when the temperature falls again the solution sets to a jelly—(this may be repeated with certain precautions) – egg albumen is soluble at ordinary temperatures, but coagulates to a mass on heating and then becomes insoluble.

When particles are exceedingly small and not much heavier than the liquid, a suspension may take a very long time to show any appreciable clearing, and may consequently appear very stable. A suspension that has settled, no matter how long it took, may be made repeatedly reversible by shaking. Among reversible colloids are aqueous solutions of tungstic and molybdic acids. As irreversible are solutions of colloidal stannic acid, ferric oxide, alumina, arsenic trisulphide, gold, silver, platinum, &c. By the addition of certain reversible organic colloids, known as Protective Colloids, inorganic hydrosols may be protected against the precipitating action of electrolytes.

The particles, besides being subject to the influence of gravity and viscosity, are electrically charged and in violent motion. This peculiar movement of particles round a central position coupled with an erratic translatory motion so well seen with the ultramicroscope, is called the Brownian movement, after Dr. Brown, the botanist, who discovered it in 1827. Most substances become negatively charged in contact with water, but the charge can be varied and even reversed by the addition of electrolytes. In this condition sols are particularly unstable and tend to precipitate. When an electric current is passed through a colloidal solution as free as possible from electrolytes, a movement of the disperse phase takes place, the positively charged phase moving towards the cathode and the negative towards the anode. To distinguish this motion from the ordinary osmotic diffusion through a membrane, this is known as Electric Osmose or Cataphoresis when a particle migrates towards the anode, and Anaphoresis when it migrates towards the cathode. This phenomenon has been used for purifying clays.

Colloidal chemistry is found to be so wide in its application and to play such an important part in nature, that at some universities it is treated as a special branch of chemistry worthy of a chair. Thus it takes part in the formation of ore deposits, and explains certain phenomena which in the past have been obscure. Interesting experiments in this respect have been made by E. Hatschek and A. L. Simon, which are given in a paper read before the Inst. Min. and Met. in 1912, and by F. Cornu and others. In ore-dressing, too, we learn much from colloidal chemistry about the vexed question of slimes, turbidity of water, frothing, &c. Colloids also play an active part in agriculture, medicine, photography, and in various industries, *e.g.*, dyeing, glass making, the manufacture of celluloid, caoutchouc, earthenware, glue, leather, paper, resin, starch, &c. It is well known that charcoal will take fusel oil from spirits, and that certain gels, such as gelatine and isinglass, will carry down turbidities in organic solutions.

E. E. Free has tabulated, with examples, Ostwald's classification of colloids (see above).

THE FIXATION OF ATMOSPHERIC NITROGEN.*

By ALLERTON S. CUSHMAN, Ph D.

A year ago I published a paper in the *Journal of the Franklin Institute* on "The Role of Chemistry in the War." This paper, which was reprinted by the U.S. Senate as Senate Document No. 340, attempted, among other things, to set forth the great importance of studying methods of fixing atmospheric nitrogen for the production of fertilisers and high explosives. In that paper the effort was made to explain in simple language the absolute dependence of our people on an adequate supply of fixed nitrogen from the danger that would ensue if war or embargo should interfere with the importation of fixed nitrogen from the nitrate beds of Chile. The air we breathe consists of nearly four-fifths of nitrogen gas, or equivalent to a weight of 33,880 tons upon every acre of land. The land needs nitrogen for the production of crops, but, except through the agency of bacteria which, curiously enough, are associated only with the root systems of beans, peas, and clovers, vegetation cannot make use of the free nitrogen of the air. Also, before it can be used for making high explosives, nitrogen must be fixed to some other element. Once thus fixed, it makes little difference to the chemist what it is joined with, as he can by one method or another manipulate it to any end product desired. Nitrogen may appear combined with other elements as a simple fertiliser for your lawn; as a deadly, treacherous explosive, an ounce of which is sufficient to wreck a building or a battleship. It may take the form of a deadly poison, cyanide, which is used to extract gold from its ores. It may be a principal constituent of a beautful dye or a beneficent medicine. It is a constituent of the wool we wear upon our backs, of the leather on our feet. Joined with oxygen, it forms the corrosive nitric acid which dissolves nearly all metals; joined with hydrogen, it forms the familiar pungent alkali, ammonia, which neutralises all acids. Fixed nitrogen in the form of protein makes the principal strength and value of the food we eat. Animals having absorbed it in part excrete the remainder in a different combination, and the manure goes back to the land to be used in part again. But there is always waste, and a large portion gets free and escapes back into the atmospheric ocean from which it originally came: hence the call upon the chemist to devise methods for its fixation.

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* Extracted from a paper on "Chemistry and American Industry," read before the Franklin Institute. From *Chemical Engineering and the Works Chemist*, vii., No. 73.

During the past year there has been much discussion and agitation over the question of nitrogen fixation. Many of the great steel and smelting companies have invested large sums of money in the installation of by-product coke ovens. One of the by-products of coke making is ammonia, and it is claimed that the fixed nitrogen from this source alone would supply all the reasonable needs of the nation. Large quantities of ammonia are, however, needed for the cooling and refrigeration of the enormous meat supplies of the world, while the chemical methods used in changing ammonia to the much needed nitric acid state of fixation present certain difficult problems which have not yet been fully worked out in this country.

By a method which is worked on a large scale at Niagara Falls, Canada, nitrogen is fixed to carbon to form a chemical compound known as cyanamide. If carbon in the form of ground coal or coke is mixed with lime and heated in an electric furnace, a carbide is formed. If air nitrogen is conducted into this substance in another furnace, the mass is converted into calcium cyanamide ($CaCN_2$), an excellent fertiliser under certain conditions. Treated with steam, this compound yields ammonia. Nitrogen can also be fixed by passing huge electric arcs or sparks through air which is conducted between terminals enclosed in furnaces of a special type. Congress has within the past year appropriated £20,000,000 for the installation of a government nitrogen fixation process, but no announcement has yet been made as to what method the government's advisers intend to select, and it is exceedingly doubtful whether the appropriation will be large enough for the purpose, or whether under our American conditions such a government plant could be operated except as a losing venture.

ORGANISATION OF BRITISH INDUSTRIAL RESEARCH.[*]

By A. P. M. FLEMING, M.I.E.E.,
Of the British Westinghouse Electric and Manufacturing Co.

THE general considerations which have last been discussed may now be applied to the particular needs of the British Empire (see CHEMICAL NEWS, cxvi., p. 4).

While there are prominent British manufacturers who appreciate the potentialities of industrial research, it must be conceded that as a body they consider such investigation to be an expensive luxury. On the other hand, during the past two years there has been disclosed in British industries an enormous latent capacity for adaptability to entirely new lines of manufacture, many of which have depended for their development upon scientific research. The research facilities, however, that have been created to such an extent during the past two years are as yet quite disproportionate to the magnitude of British industry, and it is highly desirable that the present awakening to the use of science should be fostered, and research facilities suitably organised.

For this purpose it is essential that any national scheme of research be designed on ideal lines to which existing organisation should be subordinated, so that in this way the development can proceed progressively until ultimately the plan is consummated.

From the standpoint of the individual firm, the most effective weapon in industrial competition is the application of new knowledge resulting from research applied to some immediate industrial problem. In pursuing an investigation, however, towards a definite goal, it is well known that many promising ramifications are often disclosed, which, when followed, lead to results that may be more valuable even than the original objective. In this way it may often happen that a research carried out in the interest of one industry may lead to results which prove invaluable if applied to some quite different industry. The higher forms of research, more especially those in the field of pure science, should therefore be carried out on national lines, so that any results that are derived can find application in one or other of the numerous national industries.

It is even more important that such research be organised on lines which will link up the scientific resources of the Empire. The work of the Institute of Science and Industry in Australia, and the research now being developed by the Canadian Pacific Railway, together with similar efforts that may be made in other parts of the Overseas Dominions, should be linked up with a national scheme in this country. (In the Australian scheme for a Commonwealth Institute of Science and Industry, each State has been requested to form a local committee, and a census of existing research work is being taken, together with particulars of work required which will help local industries. Some researches have already been initiated in connection with mining and agriculture. Several of the Dominions are considering schemes for co-ordinating their work on similar lines).

Apart from the interchange of scientific knowledge, such an Imperial scheme would assist the utilisation of raw materials, and in this way foster the development of the natural resources of the Empire. It is quite as important for manufacturers in Great Britain to interest themselves in any means which will improve and cheapen their raw material supplies as it is to direct scientific methods to the cheapening of manufacturing processes. An Imperial research organisation might not only result in the development of means for cheapening the production of raw materials, but also where new materials are discovered in the Overseas Dominions, assist in finding suitable outlets for their use.

An important consideration affecting industrial conditions after the war is that considerable manufacturing resources, comprising plant, machines, tools, and trained labour, will have accumulated, some of which may be turned to national benefit if they can be adapted to the manufacture of products hitherto obtained from abroad. In thus developing new lines of manufacture organised research may be of very considerable benefit. In order thus to meet international competition it is necessary to bring each manufacturing process to the highest degree of efficiency by the elimination of haphazard and wasteful methods.

With regard to the financial aspect of research, experience in the States shows that the efficiency of a well-organised laboratory increases considerably with its size, and moreover, only the large laboratories can employ methods of full-scale manufacture, which not only materially assist in the efficient development of new products, but also secure considerable revenue from the sale of commodities produced in this way. Thus the annual maintenance cost of the laboratory of the Eastman Kodak Company is £30,000, representing less than 1 per cent of the annual profits of the company.

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[*] Published for the Department of Scientific and Industrial Research by His Majesty's Stationery Office.

Viewing the American experience in the light of the considerations described above, the following seem to be the most important of the alternative schemes of research that might be employed in Great Britain:—

(*a*) Research laboratories in individual works.
(*b*) Research laboratories for a group of works in the same industry.
(*c*) The centralisation of research in the universities or colleges.
(*d*) An Imperial centralised laboratory for the whole of industry.

(*a*) Individual Works Laboratories.—The most effective way of conducting industrial research would be to equip each works with its own laboratory. By this means the most intimate needs of the firm could be studied and effectively dealt with, and such a close combination of works, organisation, and scientific investigation would probably result in a number of very efficiently conducted firms. It is clear, however, that only the largest works could support laboratories on an extensive scale. An enormous amount of over-lapping would occur, since each laboratory in the same industry would probably carry on very similar work; most firms could not stand the financial burden of such a laboratory; there would be an insufficient number of really first-class research men available to staff such laboratories; and it would hardly be practicable to carry out investigations of a purely scientific character, since the possibilities of turning a large part of the results of investigations to account in any one firm or industry would be comparatively small. Further, while by such means individual firms would be able to compete keenly with each other, their scientific resources would not be organised in the best way to meet competition in international markets.

Complete research laboratories in individual works only appear possible in the case of very large organisations, although, as noted later, individual laboratories adapted for dealing with immediate needs are highly desirable when operated in conjunction with a larger research scheme.

(*b*) Research Laboratories for a group of Works in the same Industry.—Different firms in the same industry employ very similar manufacturing facilities, and in order that the greatest possible improvement can be made in tools, methods, and processes, it is desirable that the various firms should pool for their common benefit all the experience and research facilities they possess that will assist this object. For this purpose a central laboratory might be arranged for each industry or for a group of similar firms in the same locality.

In those cases where firms have secret processes in connection with which investigations are required, these would be carried out by each firm on its own account. Many such processes, however, are of much less importance than is commonly supposed, and the experimental work thus involved would probably represent not more than a small portion of the total research requirements.

Such arrangements are already in vogue to a limited extent in this country; for instance, a central laboratory for research work is maintained in the Sheffield district, where two of the largest steel firms in intimate commercial alliance support a common research laboratory. In other cases facilities for common research have followed on the fusion of the commercial interests of two separate firms, as has occurred in the pottery district. While it may be argued that the pooling of resources may entail some self-sacrifice on the part of larger firms, from which their smaller competitors would benefit, this is probably not a very important matter, since many processes could for financial reasons only be taken advantage of by the largest firm. In any case, however, while such combinations might in the case of some firms involve a temporary loss, improvements arising from joint research would probably enable every firm to recoup far more than it expends, owing to the increased amount of business and greater working economy arising from the application of the discoveries made. The time was never so opportune for such co-operation, and never have competitive firms been so ready to share mutual interests.

(*c*) The Centralisation of Research in the Universities and Colleges.—The most extensive facilities for research in this country are at present possessed by the technical colleges and universities, and these are to some extent employed for dealing with miscellaneous investigations required by local industries. These facilities might be arranged so that each university served as a research station for one or other of the principal industries.

There are, however, many objections to this course. The function of the modern university is to educate, and its equipment and staff should be directed primarily to this end; the staff is not as a rule intimately in touch with industry, and the amount of research necessary for the industries of this country is far beyond all the resources of the universities. On the other hand, research is one of the finest possible means of educating young men for industrial employment, and consequently every encouragement should be given to graduates to pursue some research work under the guidance of an experienced experimentalist. For educational purposes the character of the research should be such as to develop the student's capacity to think for himself and increase his powers of observation and logical deduction.

At the present time, with the exception of the work of the National Physical Laboratory, most research in pure science is carried on in university laboratories, and such work is eminently suited to the capacity of the university staff. From the experience of the States it is clear that to be most effective in an industrial sense research investigations should be undertaken by a staff specially devoted to the purpose, and as far as possible also with equipment not required to be used for teaching purposes. In such cases there appears to be very little to be gained by attaching such special research laboratories or experiment stations to the universities. They might equally well be placed at other and possibly more convenient centres of industry.

(*d*) A centralised Imperial Research Laboratory for the whole of Industry.—The single laboratories dealing with the research requirements of each industry, such as outlined under (*b*), might all be grouped together in one centre—say the Midlands—and controlled by a board largely represented by manufacturers.

Such a combination would possess many advantages over separate laboratories. For instance, the cost of maintenance would be less, and through the common use of library, power supply, machine and other workshops, the first cost would also be lower. By far the greatest advantage, however, would be the benefits derived from the corporate life of such an institution, and the free interchange of experience and discussion of research work between the staffs of the various industrial sections. As already pointed out, in the pursuit of an investigation much new knowledge may be disclosed which has an important bearing on industries quite different from that of the original objective. In a laboratory confined to the needs of a single industry such new knowledge might be entirely lost, or if put on record might not come to the notice of those to whom it would be of the utmost benefit. In the centralised institution such a risk would be reduced. Further, such a laboratory would be best adapted for co-operating with the research institutions in the Overseas Dominions, and in fact would serve as a scientific focus for the whole Empire.

The staff of the laboratory would comprise a senior grade, representing the directors or heads of each industrial division; an intermediate grade, representing the principal body of research men; and the juniors, who would principally consist of graduates recently drawn from the universities. The senior staff would be permanent. The intermediate men would be continually migrating into industry as their value to manufacturers became appreciated, and this tendency would be encouraged so as gradually to permeate industry with well-trained scientific men. The junior staff would be permitted to employ part of their time in the laboratory in preparation for higher degrees, and in this way their appointment would be equivalent to a fellowship such as that tenable in some universities for post-graduate research, with the advantage that the training period would be spent under first-class research men, and the work undertaken would in most cases be of live industrial interest. The juniors would in course of time be promoted to the intermediate work.

In order to utilise every scientific asset the staff and facilities of the universities and of private research workers would be registered and incorporated as auxiliary to the central laboratory. The university staffs could from time to time for convenient periods take up research work in the central organisation itself, and in this manner keep closely in touch with modern progress.

While the function of the laboratory would be primarily to deal with problems confronting manufacturers, a considerable amount of original research in pure science would need to be done. On the other hand, the laboratory should be provided with means to carry on the actual manufacture of new products until this is undertaken by a regular commercial concern. While the first cost and the maintenance for some years would have to be provided out of public funds or by levy on the profits of industry, the institution ought to become self-supporting in time from the sale of products manufactured and from the licenses granted to manufacturers in connection with new or improved materials, processes, or tools.

Under present manufacturing conditions it frequently happens that the user of materials has to carry out the research necessary for their improvement. Fundamentally this practice is wrong, and such work should be carried out by the supplier. With the help of a centralised institution it would be possible for each branch of every industry to have its own research carried out there under the guidance of its governing body or trade association.

The importance of the collation of all scientific information, not only that pertaining to contemplated research, but also that of use in industry generally, has already been alluded to. The centralised organisation affords the best possible means of doing this, and also of disseminating it to those to whom it will be the greatest value. The laboratory would also issue bulletins of the work it carries out, and might also undertake the preparation of text-books in the most important and advanced branches of technology. The heads of the different sections of the laboratory would require to keep in close touch with the firms of the industry they represent, in order to carry out where necessary full-scale manufacturing experiments in works, and with the National Physical Laboratory, which would deal with all matters pertaining to standards and research connected therewith.

The establishment of such an organisation would tend to cause firms to instal their own laboratories in co-operation with the central laboratory for dealing scientifically with manufacturing troubles and special research problems incidental to their own products.

Conclusions.

The most important conclusions that emerge from the above facts and considerations may be shortly stated.

Industry is the basis of national prosperity, and every resource should be used to facilitate its progress. The instances which have been given above show that in this respect research is of the utmost importance, and it must be regarded as an indispensable weapon wherewith to meet international competition. The success, however, of any comprehensive scheme of research depends largely upon the attitude of the manufacturers, and it is therefore of high national importance that they should not only appreciate the value of the application of science in industry, but also co-operate in assuring that it is applied systematically and sufficiently. Among the questions that arise immediately out of the need for industrial research is that of the education and training of men for all grades of industrial employment. The full benefits of scientific investigation will not be obtained unless the results are applied by suitably trained men. There is urgent need for consideration on national lines of means for the better education and training of youths who will be the future skilled workmen; and the demand expressed by many for a more important place for science in education needs no emphasis. It is not less necessary to give attention to the scientific training of those who proceed to the higher positions in industry from the universities, and particularly to impart to such students a thorough knowledge of the fundamentals of manufacturing economics. The development of research on a large scale, and the consequent possibilities of absorbing and lucrative employment, will tend to attract to the ranks of industry many of the ablest young men who nowadays enter non-productive professions. In this way their value from a national point of view will be immeasurably increased.

Though the investment involved in providing wide facilities for industrial research will be remunerative, and may be indispensable to the prosperity of individual industries and even of the nation itself, it must involve large sums of money, some part of which can bring no immediate result. Such measures cannot be introduced successfully unless they are supported by public opinion; and a great need therefore exists for bringing continually before the public the necessity of industrial research, with its possibilities and benefits. To this end the facilities afforded by the daily press, and particularly by the trade, technical, and scientific press, should be fully utilised, and, further, these means might well afford channels not only for the distribution of information and knowledge to the general public, but for receiving from the latter suggestions and expressions of need for promising lines of investigation. In this manner public opinion may be developed along desirable lines and some latent scientific talent disclosed.

A new phase in industrial and economic life is commencing, and its development will be governed very largely by the extent to which new scientific knowledge is obtained and turned to the benefit of mankind. It is by the progressive use of research, every advance of which opens up ever wider industrial possibilities, by the fullest employment of the nation's inherent manufacturing capacity, and by the wise co-operation of labour and capital, that the prosperity of this country can be assured.

I desire to express my grateful thanks to the large number of American scientists connected with the various manufacturing corporations, universities, State and other scientific institutions referred to in this memorandum, not only for the personal facilities accorded to me when visiting their laboratories, but also for their courtesy in supplying me subsequently with much important information; also my indebtness to the Management of the British Westinghouse Electric and Manufacturing Company for the permission—readily accorded—to make known the information thus obtained.

THE ESTIMATION OF XYLENE IN SOLVENT NAPHTHA.

By PERCY E. SPIELMANN, Ph.D., B.Sc., F.I.C.,
and
F. B. JONES, B.A. (Cantab).

The difficulty attendant on this estimation is due to the fact that xylene itself consists of three isomers of different boiling-points and specific gravities, and that it exists as such in a complex mixture of cumene, trimethylbenzenes, and other substances which boil gradually up to 170° C. and over. It has been found that if the benzene, toluene, and xylene be completely removed by careful and repeated fractionation from different makes of solvent naphtha, and the fraction of the residue boiling from 143—170° C. be examined in a constant boiling-point apparatus (such as that devised by Northall Laurie in connection with his estimation of toluene) the constant boiling point obtained scarcely varies with the different makes.

Commercially pure xylene, fractionated and collected between 138 and 143° C., gives in the same apparatus the constant boiling point of 139·15 C. It becomes possible, therefore, from examination of known mixtures of xylene with the 143—170° C. residue, to construct a curve by means of which the composition of unknown similar mixtures may be found from their boiling points.

100 cc.—or 200 cc. if necessary, for Colman's analysis —of solvent naphtha, accurately measured, is distilled over a Young 12 pear head at the usual rate of one drop a second. The fractions up to 138° C. and from 138° C.—170° C. (all temperatures being corrected) are collected in separate cylinders and measured.

The benzene, toluene, and xylene in the first fractions (up to 138° C.) are estimated by Colman's methods for examining toluols and solvent naphtha. The xylene in the 138—170° C. fraction is evaluated by taking the boiling-point in the constant boiling-point apparatus, and referring to the appended graph.

All possible care must be taken to get an accurate reading for the boiling-point, corrections being made for barometric pressure, thermometer error, and unexposed stem, as is customary in such determinations. A steady temperature is usually attained after about twenty minutes' boiling at such a rate that the liquid condensed from the vapour drops back from the end of the condenser at the uniform rate of one drop a second. After constancy is approximately attained, there is a slow rise in temperature on continued boiling, due, apparently, to the warming up of the unexposed stem of the thermometer, and of the end of the reflux condenser.

The accuracy of the boiling-point curve may be taken as ± 1½ per cent, when the xylene content of the 143—170° C. fraction is above 50 per cent, but owing to the divergence of boiling-point of the "higher than xylenes" there may be an error of more than ± 2½ per cent when only small quantities of xylene are present. As, however, the average quantity of xylene in solvent naphtha is about 60 per cent, the region of the curve showing the maximum error will not be employed in practice.

Determination of the composition of mixtures of xylene with the 143—170° C. residue from three makes of solvent naphtha, other than those from which the curve was constructed :—

	Taken (xylene per cent).	Found (xylene per cent).
1.	11·6	14·0
2.	29·3	28 8
3.	66·9	65·5

For the sake of completeness, a full example is given of the examination of a sample of commercial solvent naphtha, including the corrections for unexposed stem and barometric pressure, and their applications.

The correction for unexposed stem may be calculated from the formula :—

No. of degrees to be added to observed reading = $0{\cdot}000143\ (T - t)\ N$.

T = observed reading.
t = temperature of external part of stem.
N = number of degrees not exposed to the vapour.

More conveniently and quickly this correction can be ascertained from a graph (Wheeler, *Journ. Soc. Chem. Ind.*, December 15, 1916).

The correction for barometric pressure is given by the equation :—

$$\Delta t = 0{\cdot}016\ (760 - p).$$

Δt is the number of degrees to be added or subtracted according to sign, and p is the corrected barometric pressure (corrected for temperature) at the time of experiment.

Example.

Volume from distillation of 100 cc. over a 12-pear bead up to 138 C. = 22·1 cc.

This 22·1 cc. was mixed with 57·5 cc. pure toluene and 20·4 cc. pure benzene, and the mixture analysed by Colman's method. The results indicated that the 22·1 cc. contained benzene, nil ; toluene, 6·2 cc. ; xylene (by difference), 15·9 cc.

Volume from distillation of 100 cc. over 12 pear bead from 138—170° C., 69·7 cc.

Boiling-point of this fraction :—

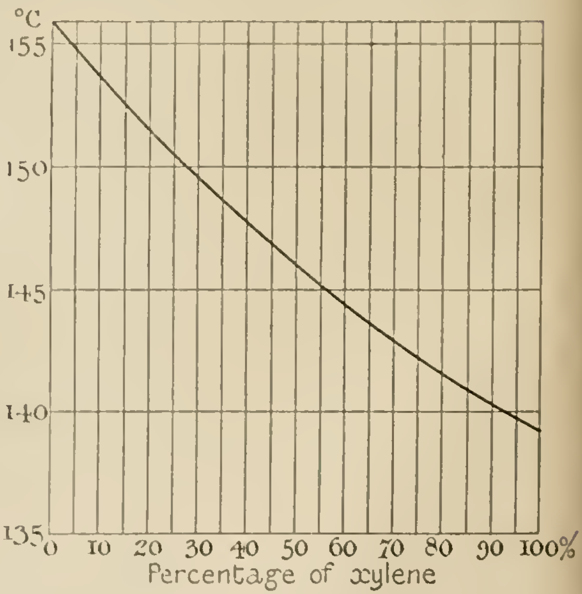
Observed reading .. .. = 141·6° C.
+Thermometer error correction .. = 141·7° C.
+Barometric correction (for 755 mm.) = 141·9° C.
+Unexposed stem correction .. .. = 143·25° C.

On reference to the curve the fraction is found to contain 67·2 per cent xylene, corresponding to the corrected boiling-point 143 25° C.

∴ Total content of xylene in the original solvent naphtha $= 15{\cdot}9 + \dfrac{69{\cdot}7}{100} \times 67{\cdot}2 = 63$ per cent.

Paraffin.

An estimation of the proportion of paraffin associated with xylene may be made by the following procedure, based closely on the method of Wilson and Roberts (*Gas Record*, Chicago ; *Journ. Gas Lighting*, 1916, p. 225 ; *Journ. Chem. Soc. Ind.*, 1916, xxxv., 684).



The quantity of the sample—100 cc. is generally sufficient—is distilled over a Young 12 pear head at the rate of one drop a second, the portion distilling between 138—143° C. (corrected) being collected separately. Ten to 20 cc. of this fraction is vigorously shaken for about forty minutes with two and a-half times the volume of weak oleum made by mixing one volume of 22 per cent oleum with two volumes of 95 per cent sulphuric acid.

The absorption of the aromatic hydrocarbons is carried out in a 100 cc. flask, of which the neck is graduated into 10 cc. and sub-divided into tenths of a cc. from the volume mark upwards. After sufficient shaking the level of the liquid is driven up into the graduated neck by the addition of a further quantity of 95 per cent sulphuric acid.

After standing—preferably overnight—the paraffin will be found to be sharply separated.

Example.

100 cc. of the solvent naphtha quoted above gave about 23 cc. between 138° and 143° C. 20 cc. of this fraction yield 2·5 per cent of paraffin residue.

This is the quantity present in 20 cc. of the xylene fraction, therefore in 63 cc. of the xylene (*i.e.*, the quantity of xylene found in 100 cc. of the solvent naphtha) there is $\frac{63}{20} \times 2{\cdot}5 = 8$ per cent of paraffin.

Therefore this particular sample of solvent naphtha contains 55 per cent of xylene, together with 8 per cent of associated paraffin.

The inquisitiveness regarding the composition of the various fractions of light naphtha, which has been occasioned by the war, has given rise to much detailed work, so that now the main constituents of the whole series of fractions from benzole forerunnings to xylene can be estimated with considerable accuracy.

Benzol Firstrunnings.—Spielmann and Butler Jones, *Journ. Soc. Chem. Ind.*, Sept. 15, 1916, p. 396.

Benzols.—Spielmann and Wheeler, *Journ. Soc. Chem. Ind.*, April 15, 1916, p. 396.

Commercial Toluols.—Colman, *Journ. Gas Lighting*, 1915-1916. Edwards, *Journ. Soc. Chem. Ind.*, May 31, 1916, p. 587. James, *Journ. Soc. Chem. Ind.*, Feb. 29, 1916. Wilson and Roberts, *Gas Record* (Chicago); *Journ. Gas Lighting*, 1916, cxxxiv., 225; *Journ. Soc. Chem. Ind.*, 1916, p. 684.

Pure Toluols (suited also to commercial quality).—Northall-Laurie, *Analyst*, 1915, p. 384.

Toluene in Solvent Naphtha.—Colman, *Journ. Gas Lighting*, 1915, p. 314.

Xylene in Solvent Naphtha.—Spielmann and Butler Jones.

—*Journal of the Society of Chemical Industry*, xxxvi., No. 9.

WAR PRODUCTS FROM PETROLEUM.

Process Secured by Germans Six Months Before War.

(*From a Correspondent*).

A process for the purification of crude petroleum, commercially economical by reason of the quantitative recovery of the solvent for future use and the extraction of valuable by-products, was the subject of an important application in the Patents Court by the Anglo-Persian Oil Co., Ltd., which has a capital of four millions (half of it held by the British Government) with controlling interest in various other oil-producing concerns.

The oil is brought to this country by tank steamers—the Anglo-Persian Oil Company owns the whole of the capital of the British Tanker Co., Ltd.—and the scheme is to treat the import here by a process which, because of its war uses, has already had the attention of the German authorities.

The method was patented by a Roumanian chemist, Lazar Edeleanu, of Bucharest, from whom, it was stated, it was bought by Gemans only in the February before the war broke out. The patent is 11140 of 1908, and the purchasers were the Algemeine Gesellschaft fur Chemische Industrie of Unter-den-Linden, Berlin. The Anglo-Persian Oil Co. applied for licence to use the patent, owned by an alien enemy.

Dr. Edeleanu states that before his patent the treatment of crude petroleum for obtaining benzine and illuminating or mineral oils had been carried out by subjecting the petroleum to fractional distillation and treating the distillates with sulphuric acid and alkalies. Where, however, the petroleum or its distillates contained large proportions of hydrocarbons poor in hydrogen the method did not give good results, and where it had been possible to obtain good products by treating with large quantities of sulphuric acid at high temperature the process was costly owing to losses in the distillates, the amount of sulphuric acid required, and the difficulty of the recovery of sulphuric acid on account of the formation of sulphonic acids.

These disadvantages the patented process obviates. The invention consists in purifying crude petroleum or products or distillates by treatment with liquid sulphur dioxide, or sulphur dioxide in the state of liquefaction. The compounds which cause colour and odour, and the matters rich in carbon in the crude petroleum, and injure the quality of the petroleum products, are found to be soluble in liquid sulphur dioxide, whereas the hydrocarbons which constitute the refined products are insoluble or largely insoluble in it.

The liquid sulphur dioxide is mixed with the crude petroleum at a low temperature—preferably below zero Centigrade—by agitators. When settlement has taken place, the solution containing the impurities is drawn off.

The recovery of the sulphur dioxide can be effected quantitatively by gassifying the liquid sulphur dioxide, and the gassification may be assisted by the use of an exhausting pump. The last trace of sulphur dioxide can be separated by washing the residues with water or aqueous solutions of alkaline substances.

Mr. Hunter Gray, who presented the applicant's case, said the advantage of avoiding sulphuric acid and wasteful tar products was recognised, together with the advantage of using the re-agent over and over again. By this process the impurities responsible for deleterious colour and smell were dissolved out, and it was convenient to use the liquid sulphur dioxide for purifying at low temperature. While primarily the patent was for getting a pure oil, the Controller of Patents would appreciate that substances might be obtained through the sulphur dioxide which would be very useful in certain other directions. He thought the Germans had their eyes on these by-products when they persuaded the patentee to sell the patent to them six months before the war broke out. He said "persuaded" advisedly, for they seemed to have been able to get it for the small sum of £500. He would write down on a piece of paper what were some of the by-products the process yielded.

Mr. Hunter Gray accordingly made out a list and handed it to the Controller, Mr. Temple Franks, and Sir Cornelius Dalton, who was sitting with him.

The Anglo-Persian Oil Co., Mr. Gray went on, had a capital of four millions—three million ordinary shares of one pound and one million participating shares of one pound, and of these the British Government held half, or two million, of the ordinary shares, and a thousand of the preference shares, and he thought they had debenture stock—199,000—with a right to elect upon the board two ex officio directors, and certain powers as regarded dealing with the business, so that the British Government could be said to be behind the application. He handed in the Blue-book which contained the agreement with the Treasury.

The Controller said he was curious to know the extent of the Anglo-Persian Oil Co.'s business ramifications.

Mr. Hunter Gray replied that they had a concession from the Persian Government for petroleum oil, natural gas, and kindred products throughout the Persian Empire, and they owned the controlling interest in the First Exploitation Co., Ltd., which was a producing Company, and 95 per cent of the total capital of the Bakhtiari Co. and the whole of the shares in the British Tanker Co., Ltd. They had important concessions for oil abroad, especially in Persia. They purified it in this country, and sold for various purposes, one of which the Controller could easily imagine having regard to the agreement. They had not purified on a large scale up to the present, but they desired to do so as soon as they obtained this licence. They had spent £25,000 on plant, and proposed to put down plant with a capacity for 40,000 tons per annum. With a yield of other products which might be permanently useful, the expenditure of £25,000 might be taken to be only a first instalment.

Mr. H. Nichols, director of the Anglo Persian Oil Co., answering the Controller, said the patent had produced a great improvement in the case of kerosine, in respect of the burning qualities of the oil, and removed the aromatic hydrocarbons which were generally the cause of filming in lamps of that class. Their chief chemist, prior to the war, was in communication with Dr. Edeleanu, and as a fellow chemist, the doctor exchanged views with him on the subject of the working of the patent. The negotiations were in respect of the Burma Oil Company, which was affiliated with the Anglo-Persian Co. The latter held a large block of their ordinary shares. In getting to work they would not have the benefit of the Doctor's experience in tuning up the plant, and that should be borne in mind in considering the question of royalty.

Dr. A. E. Dalston, the applicant's research chemist, explained that they looked to the system not so much to lessen the price as to give a better article. There were certain oils from different parts of the world which contained these carbons; in the oils of other countries they were either absent or not so objectionable. The oil was used mainly for lighting purposes and was not ordinarily useful for oil engines. The actual operation of the plant might work out at five shillings a ton, with the use of the materials. As to the by-products, a large amount of experimental work would have to be done in translating from the laboratory to the manufacturing scale. The Anglo-Persian Oil Co. wanted a process by which the liquid sulphur dioxide would be given back again. The liquid sulphur dioxide plant could not be used for anything else.

The Controller said the process was a valuable one and should be put to use as soon as possible, and the applicants would be notified by the Board of Trade at an early date as to the issue of their licence.

THE LATEST INFORMATION AS TO CROPS OF 1917.

The crops have been very much favoured during May by the increasing temperature with the intermittent rainfall, prevailing in Western Europe and on the shores of the Mediterranean.

Vegetation in France, Great Britain, and Italy, previously so backward, has been able to make up the greater part of the time lost owing to the rigours of the earlier months of 1917. Spring sowing has almost everywhere been carried out in favourable surroundings, and the young plant is generally reported as healthy and vigorous.

In Northern and Central Europe, especially in Luxemburg and the Netherlands, the drawbacks resulting from the length and severity of the winter are still seriously felt. Spring sowings have taken place in Luxemburg in normal surroundings; their condition in the Netherlands is only moderate. In Switzerland, in spite of the recent warmer weather, the outlook for the winter crops is under average, but that for the spring sowings may be considered as normal. In the greater part of European and Asiatic Russia, temperature below the normal has hitherto prevailed. But despite these unseasonable chills, the situation appears to be favourable as a whole, and an area under spring crops equal to last year was expected. Drought and wind had hindered the development of the spring crops in some districts of Siberia.

In Canada, spring sowing was practically finished, and the area under wheat compares favourably with that of 1916. Although in the United States, the winter crops suffered injury, from the severity of the season and the violent winds, to such an extent as to cause the abandonment of nearly one-third of the area sown with wheat, the weather of the last few weeks has been so favourable that the wheat crop as a whole promises a larger yield than that of last year. In British India the outlook is very good, while that of Japan is an average one. In Egypt, the results of the crop are considered to be satisfactory.

From advices to hand up to the present at the International Institute of Agriculture at Rome as regards official forecasts of the wheat crop of 1917, that of France is 44,000,000 quintals, or three-fourths of the crop of 1916.

In the United States, taking winter and spring wheat together, the forecast is for 178,537,000 quintals, which indicates a larger yield than that of 1916 by 21½ per cent, but smaller than the average from 1911 to 1915 by 18 per cent. In British India, the position is excellent, since the crop of 1917 amounts to 103,230,000 quintals, or nearly 20 per cent over that of 1916, and 5 per cent more than the average. In Japan, the estimate for 1917 is 7,221,000 quintals, or 94 per cent of the crop of 1916, and 108 per cent of an average.

As regards those countries which have not sent numerical data as to their prospective yield to the Institute of Agriculture in Rome, it is as well to ascertain whether the area in 1917 is so extensive as to allow of satisfactory yield. We note that in Spain the area is very slightly larger than in 1916, and 6 per cent over the average. On the other hand, in Algeria it is 4 per cent less than in 1916, and 8 per cent under the average, and in Tunis it is 12 per cent below that of 1916, though slightly above the average. In Canada the area cultivated in 1917 is reported as 4 per cent larger than in 1916, and 16 per cent above the average.

With regard to forecasts for the cereals other than wheat, at present the United States is the only country that has supplied figures. These are—

14,707,000 quintals of rye (112 per cent of the crop of 1916, and 140 per cent of an average).

46,592,000 quintals of barley (118 per cent of the crop of 1916, and 108 per cent of the average).

210,452,000 quintals of oats (110 per cent of the crop of 1916, and 112 per cent of the average).

—*International Institute of Agriculture, Rome.*

PROCEEDINGS OF SOCIETIES

ROYAL SOCIETY.

Ordinary Meeting, June 28, 1917.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

"*A Contribution to the Study of the Magnetic Properties of Manganese and of Some Special Manganese Steels.*" By Sir Robert Hadfield, F.R.S., Ch. Chéneveau, and Ch. Géneau.

1. The research has had for its object the investigation of the mass-susceptibility of manganese metal, and of certain of its alloys with iron and other metals. The work was carried out on a Curie-Chéneveau magnetic balance.

2. Manganese itself, when free from occluded gases, is para-magnetic, its value of χ being $+11\cdot0\times10^{-6}\pm2$ per cent. This corresponds on Weiss's theory to a number of magnetons equal to 6. The removal of occluded gases is essential as the ferro-magnetic properties of certain specimens of manganese is shown to be due to the presence of hydrogen.

3. The manganese alloys investigated, with one exception, are all para magnetic, χ varying from $17\cdot0\times10^{-6}$ to $259\cdot0\times10^{-6}$. The exception mentioned is a silico-manganese steel containing 6 per cent of silicon, which is distinctly ferro-magnetic.

4. An endeavour is also made to correlate the values of the mass-susceptibility with the composition of the alloys. In this connection it has been shown that the quantity of manganese within the limits investigated has very little influence upon the susceptibility, whilst increase of carbon

tends to decrease it. In general it is concluded that in these special steels the susceptibility decreases as the carbon-manganese ratio increases.

5. The carbon-manganese ratio being constant, addition of chromium, nickel, or tungsten raises the susceptibility.

6. The addition of copper to a manganese-nickel steel also raises the susceptibility—this notwithstanding the diamagnetism of copper.

"*Note on the Specific Heat of Water.*" By W. R. Bousfield, F.R.S.

Replying to criticisms by Callendar (Bakerian Lecture, *Phil. Trans.*, A, 1912, ccxii., p. 1) on the methods for investigating the specific heat of water described in a former paper (W. R. Bousfield and W. Erfc Bousfield, *Phil. Trans.*, A, 1911, ccxi., p. 199), it is pointed out that the observations of Callendar do not substantially affect the question as to which figures are more correct in the lower range of temperature from 0° to 40° or 50°. Callendar and Barnes differ from other observers in placing the minimum value for the specific heat of water in the neighbourhood of 40°, whilst other observers put it at about 25° C.

In an investigation into the specific heats of solutions of KCl and NaCl, it was necessary to re-determine the capacity of the calorimeter between 0° and 39°. The figures for the mean capacity for the three ranges of temperature calculated from the respective figures for the specific heat were:—

	0–13°.	13–26°.	26–39°.
Bousfield..	839	857	876
Callendar and Barnes ..	824	815	849

As the specific heat of glass steadily increases with rise of temperature, it is obvious that the second set of capacities is inadmissible. The irregularity of the second set is ascribed to the shifting of the minimum, and the regularity of the first set supports the view that the minimum is in the neighbourhood of 25°. Further support is given to this by the fact that the first set of capacities brings out the specific heats of concentrated KCl and NaCl solutions as following a nearly linear temperature law.

"*The Specific Heat of Aqueous Solutions with Special Reference to Sodium and Potassium Chlorides.*" By W. R. Bousfield, F.R.S., and C. Elspeth Bousfield.

The specific heats of solutions of NaCl and KCl ranging from saturated solutions to quarter-normal solutions at mean temperatures of 7°, 20°, and 33°, have been determined by the method and apparatus used for the determination of the specific heat of water, and described in a former paper (*Phil. Trans.*, A, 1911, ccxi., p. 199). The corresponding densities have also been determined. The relation of the specific heat of the solution to the specific contraction of the water is studied, and it is shown that the specific heat of a series of solutions of different concentrations may be reckoned on the hypothesis that the specific heat of the solute is constant, whilst the mean specific heat lowering of the water is proportional to the specific contraction of the water.

The temperature variations of the specific heats of the solutions are also compared with the temperature variations of the specific heat of water. The minimum value on the temperature-specific heat curve, which occurs at about 25° in the case of water, disappears altogether in solutions of half normal to normal strength. This curve for the most concentrated solutions becomes a straight line.

Incidentally, a relation emerges between heat of solution and contraction which may be expressed as—

$$\left(\frac{d\,Q}{d\,\theta}\right)_{H} = L\left(\frac{d\,\chi}{a\,H}\right)_{\theta} \;;$$

where Q is the heat of dilution per grm. of added water and $d\chi\ aH$ is the contraction per grm. of added water, H being the weight of water per grm. molecule of the solute, and θ the temperature, while L is the constant which expresses the ratio of specific heat lowering to specific contraction.

"*The Rankine Trochoidal Wave.*" By Sir George Greenhill, F.R.S.

The Rankine trochoidal wave (*Phil. Trans.*, 1863), either as rollers or a starting wave, can be divided up by vertical planes perpendicular to the wave crest into compartments, and the compartments sheared along each other.

The investigation is made of the extra field of force in addition to gravity when the shear is made continuous and the planes removed in order that the continuity of pressure should be preserved in the interior of the water, and for the new wave motion to persist.

Also when the planes stand over to the vertical and the circular orbits in the roller are in parallel planes.

A geometrical investigation is added of the molecular rotation in the interior of the Rankine wave.

"*The Tribo-Electric Series.*" By P. E. Shaw, D.Sc.

1. The tribo-electric series, in which solid materials are arranged in order according to the charge they acquire when rubbed together, is reliable with due precautions. In the table are shown the common solid metallic and non-metallic elements interleaved with a great variety of other compound materials.

2. Most solids are found to alter their place in the series if heated above a certain temperature which is specific for each material. This temperature is called the critical temperature. The surface in its new condition is termed abnormal.

3. The series may be divided into an upper Group A and a lower Group B. It is found that these groups have tendencies contrary to one another as the surfaces of the materials are rendered (*a*) matt, or (*b*) abnormal, or (*c*) pressed, or (*d*) flexed). If under any of these agencies Group A becomes more + forming, Group B becomes more − forming, and vice versa. This principle is here called duality. It is possible that the phenomena observed by Hésébous with radium may be another case of this duality of action, for glass is in Group A and ebonite in Group B.

4. Anomalous effects are observed when liquid mercury is used as one of the materials, its behaviour being quite unlike that of solid surfaces.

5. As to theory, it is suggested that the prevalent idea that the electric double-layer existing at the surface of solids has the − layer outermost in all cases, is incorrect. Normally the materials in Group A would have − outermost, those in Group B having + outermost. Orientation of surface atoms would give rise to changes in the disposition of the two electric layers and so account for observed effects.

6. Tribo-electricity undoubtedly affords a means, of extraordinary delicacy, of discriminating between materials apparently alike. Two instances are seen in the group of furs and the group of woods.

"*Nature of the Ions Produced by the Spraying of Water.*" By J. J. Nolan.

Part I. gives an account of the determination of the mobilities of the very mobile ions produced by the spraying of water. Groups of ions are found, positive and negative, some of very high mobility.

In Part II. the less mobile ions described in a previous paper are discussed. Treating the ions as minute spheres of water, it is shown that their sizes as deduced from an empirical modification of Stokes' law would agree with the sizes calculated from the ordinary theoretical mobility formulæ. Certain evidence, however, tends to show that the larger of these ions are not simple spheres of water, but that they consist of loose groupings of various numbers of some smaller water-globules. Both views as to the constitution of the larger ions are considered. On either view the various ions can be explained by assuming that each ion is formed by the combination of a certain number of ions of the next smallest size. The loose-grouping view of the larger ions—in addition to other advantages—admits of a greater uniformity in the process of aggregation by which the ions are supposed to be built up.

In Part III. it is shown that the very mobile ions can be accounted for by supposing that they consist of aggregates of various numbers of water-molecules, the numbers of molecules in the various ions being related to one another in a regular way. Some of these ions have the same mobility as ions produced in air by X rays, &c. It is suggested that the ordinary gaseous ion consists of a group of water-molecules, the size of the group depending on the degree of moisture of the gas. Evidence from various sources is adduced in support of this view.

"*The Absorption Spectra and the Ionisation Potentials of Calcium, Strontium, and Barium.*" By Prof. J. C. McLennan, F.R S.

"*Geotropism and the Weber-Fechner Law.*" By James Small.

"*The Isolation from Peat of Certain Nucleic Acid Derivatives.*" By Prof. W. B. Bottomley.

CHEMICAL SOCIETY.

Ordinary Meeting, June 21, 1917.

Dr. Alexander Scott, M.A., F.R.S., Past President, in the Chair.

Reference was made to the loss sustained by the Society, through death, of the following Fellows:—Edward William Lanchester Foxell (fell in action); George Carrington Carrington.

The Chairman drew the attention of the Fellows present to a communication received from the Committee of the Van't Hoff Fund for the endowment of research in pure and applied chemistry founded in June, 1913. The amount available for distribution during 1918 is about £150. A Committee, consisting of Prof. A. F. Holleman (President), Prof. S. Hoogewerff, Prof. A. Smits, and Prof. E. H. Büchner (Secretary), has been appointed to award grants. Applications should be sent before Nov. 1, 1917, by registered post, to "Het Bestuur der Koninkklyke Akademie van Wetenschappen; bestend voor de Commissie van het 'Van 't Hoff-fonds' Trippenhuis, Kloveniersburgwal, te Amsterdam." Every applicant is requested to submit a detailed account of the manner in which he proposes to expend the grant, and to state the reasons for which he makes his application.

Papers embodying the results of the research may be published in any journal, but acknowledgment must be made of the source of the grant. Copies of papers containing the results of the research must be forwarded to the Committee.

Certificates were read for the first time in favour of Henry Joseph Cunningham, B.Sc., 25, St. Thomas's Street, Newcastle-on-Tyne; Arthur Doulton Dibley, No. 3 Hostel, Nancot Royal, Hawarden.

Dr. C. H. Desch and Dr. G. Senter were elected Scrutators, and a ballot for the election of Fellows was held. The following were subsequently declared duly elected as Fellows:—Montague Aldridge, M.A.; Arthur John Daly, B.Sc.; Manmatha Nath Das, B.A.; David Richard Davey; James Nelson Edmund Day; James Garfield Detwiler, B.Sc.; Carleton Ellis; Albert Henry Frankland; Frederic William Gamble; Harry Gollop, B.Sc.; Hubert Henry Hazel, B.A.; Kenneth Claude Devereux Hickman; Henry James Hinks; Cuthbert Baring Horwood, B.Sc.; George Inglis Hudson; William King; Frederick George William Knapman, B.Sc; Robert Illtyd Lewis, B.Sc.; Louis Frederick William Leese; Joseph Patrick Madden; Joseph Harold Mandleberg, B.A.; Albert Edward Mills; John Montgomery; Leslie O'Brien; James Patrick O'Callaghan; Herbert Skellon, B.Sc.; Nicholas Karrachy Smith, B.Sc.; Herbert Swann, B.Sc.; Cedric Gerard Verver; Michael J. Walsh, M.Sc.; Howell Williams; Percy Noel Williams, B.Sc.

The following papers were read:—

"The Conversion of Ortho-nitroamines into *iso*-Oxadiazole Oxides and of Ortho-nitrosoamines into *iso*-Oxadiazoles." By A. G. Green and F. M. Rowe.

"Catalysis. Part III. Some Induced Reactions." By N. Dhar.

"Catalysis. Part IV. Temperatore-coefficients of Catalysed Reactions." By N. Dhar.

THE ASSOCIATION OF SCIENCE, LIMITED.

At a General Meeting of the Association of Science, Ltd., held on July 11, 1917, it was unanimously resolved:—

1. That a liberal education should in all cases include sound elementary instruction in Biology, Botany, Chemistry, and Physics.
2. That the status of Science Masters and Teachers should be substantially improved.
3. That the position and payment of Scientific Workers are, at present, in general, inadequate, and ought to be raised.
4. That increased opportunities and incentives for scientific studies and research should be provided for persons above school age, so as to be available for those who are employed during the greater part of the day in various avocations.

And I was directed to forward to you a copy of these resolutions.—Hugh Woods, M.D., Secretary.

NOTICES OF BOOKS.

Manual of Chemistry. By W. Simon, Ph.D., M.D., and Daniel Base, Ph.D. Eleventh Edition. London: Baillière, Tindall, and Cox. 1917. Pp. xvi. + 648. Price 18s.

In the eleventh edition of this much used work, many alterations and improvements have been made, and students of pharmacy, dentistry, and medicine will find it an invaluable guide, specially adapted for the use of those who are beginning the study of the science. The text has been thoroughly revised, and some parts of it have been carefully rearranged and added to, while in other places a certain amount of deletion has been performed. Thus, the chapters on light and electricity have been removed from Section I., though the articles on the spectroscope and polariscope have been retained in the appendix. Much new matter has been added to the sections on the non-metals and also to the last part which deals with organic chemistry. The book thoroughly deserves the confidence it has inspired, and the eleventh edition will, undoubtedly, be as highly valued as its predecessors.

Annual Chemical Directory of the United States. Edited by B. F. Lovelace. Baltimore, U.S.A., Williams and Wilkins Co. 1917. Pp. 305+60. Price 5.00 dols., post paid.

This first annual issue of the "Chemical Directory of the United States" contains comprehensive lists of dealers in chemicals and chemical appliances of all kinds, and of professional chemical firms, consulting and analytical chemists, and chemical engineers. American and foreign laboratories are enumerated, as well as experimental stations in the United States and abroad, and full lists of journals and publications are included, with notices of important new books and fresh editions. A very short summary of developments in chemistry during 1916 is also given, containing some notes on problems connected with the manufacture of dyes, the extraction of potash from various sources, and the fixation of nitrogen. For the investigation of this last subject and the erection of a Government plant, Congress, in the summer of 1916, appropriated a sum of 20,000,000 dols. The directory appears to be well planned and conveniently arranged, and it contains a large amount of information likely to be useful to chemical manufacturers, merchants, and engineers.

THE CHEMICAL NEWS

Vol. CXVI., No. 3009.

A CONTRIBUTION TO THE ENERGY THEORY OF MATTER.

By H. STANLEY REDGROVE, B.Sc. (Lond.), F.C.S.

In an article entitled "The Claims of Thermo-Chemistry," published in *Knowledge* for July, 1910 (vol. vii., new series, pp. 227-230), I pointed out that every chemical compound could be regarded not only as a complex of inertia units (atoms), but also as a complex of energy units (valency-bonds) differing quantitatively and qualitatively from one another. In that article I emphasised the importance of the latter point of view and devised a system of formulæ specially adapted for this purpose; thus the formula for ethyl alcohol C_2H_5OH, for example, which contains one C.C bond, five C.H bonds, one C.O bond, and one O.H bond, is written—

$$(C.C)(C.H)_5(C.O)(O.H),$$

whilst that of methyl ether $(C_2H_3)_2O$, which contains six C.H bonds and two C.O bonds, is written—

$$(C.H)_6(C.O)_2$$

In the present article it is proposed to prove and illustrate what I claim to be a hitherto unrecognised law, namely, that every physico-chemical property, which is "additive" in the broadest sense of that word, is a function of the number and sort of valency-bonds or energy units of which the molecules of the bodies exhibiting the property in question may be regarded as complexes.

First of all, however, a word or two is necessary regarding the significance of the term "additive." The one property which is, so to speak, ideally additive is molecular weight; as we know, the molecular weight of a compound is exactly equal to the sum of the atomic weights of its constituents. Kopp found that a similar law held good to some extent for molecular volume, and, as research proceeded, other properties were found to be additive also, such as molecular refractivity and dispersion (Brühl), and molecular heat of combustion and formation.

It became evident, however, that the mode of combination exercises a considerable influence on the values of the elements; thus, constants calculated for saturated carbon compounds do not hold for unsaturated ones, different values have to be assigned to oxygen according to whether it is etheric, carbonyl, or hydroxyl oxygen, and so on. The difficulty was to some extent obviated by introducing corrections fo certain forms of valency-bonds, such as "double" and "treble" carbon links. But in a paper published in the Chemical News in 1907 (vol. xcv., p. 193) I pointed out that if values must be assigned to certain valency-bonds, it is only in accordance with scientific procedure to treat every valency-bond as exercising some influence. At any rate, I argued, there is no justification, in the absence of evidence, to suppose the influence of certain bonds to be nil; and I proved in the paper in question that, discarding this untenable hypothesis, the values of the simple constants for the atoms and valency-bonds are, in general, unobtainable at the present state of knowledge. I showed, however, how certain complex constants could be calculated and used to determine questions of constitution, &c., and, in a series of papers, applied the method very fully to the heats of combustion and heats of formation of various carbon compounds as well as to molecular refractivities and dispersions of hydrocarbons.

It may be taken as proved, therefore, that such physico-chemical properties are primarily functions of the number and sort of atoms comprising the bodies exhibiting them together with the number and sort of valency-bonds between such atoms. Now, if we know the atoms comprising the molecule of a body, it by no means follows that we therefore know the valency-bonds. C_2H_6O, for instance, may be ethyl alcohol, C_2H_5OH, containing one C.C., five C.H., one C.O, and one O.H bonds, or methyl ether, $CH_3.O.CH_3$, containing no C.C, six C.H, two C.O, and no O.H bonds, and so on. On the other hand, if we know the valency-bonds in a compound, although some ambiguity may still exist as to the exact arrangement of the atoms, we can deduce with certainty the number and sort of atoms present; thus, if we are told that the molecules of a body each contain only two C.O and six C.H bonds, then they must each contain two C atoms, six H atoms, and an O atom, the body being methyl ether, $CH_3.O\ CH_3$. It follows, therefore, that the number and sort of atoms comprising a molecule may be regarded as a function of the number and sort of valency-bonds, which may also be said to compose it if it is regarded as an energy-complex. It follows that every additive physico-chemical property is a function of the number and sort of valency-bonds in each molecule of the body exhibiting the property in question. And it should be evident that this statement holds more accurately than that underlying the older method of calculating physico-chemical constants—namely, that additive properties are atomic functions—since the inevitable valency-corrections of this method are obviated.

In order to make the argument clearer, I propose here to give a mathematical proof of the law for the hydrocarbons, a proof which, it will be readily seen, can be easily extended to include any other classes of carbon compounds, with which I am mainly concerned.

I have shown (*op. cit.*) that every hydrocarbon must conform to the formula—

$$n\mathrm{C}+2(n+1-a-2b-p)\mathrm{H},$$

where $n+p-a-b-1$ is the number of C.C bonds in each molecule, a the number of C:C bonds, and b the number of C $\vdots$ C bonds. The body, of course, will also contain $2(n+1-a-2b-p)$C.H bonds per molecule. Using the same symbols to stand for the effects towards the physico-chemical property in question of the atoms and bonds, it follows that the value of this property of the "general" hydrocarbon is—

$$n\mathrm{C}+2(n+1-a-2b-p)\mathrm{H}+2(n+1-a-2b-p)\mathrm{C.H}+\\(n+p-a-b-1)\mathrm{C.C}+a\mathrm{C{:}C}+b\mathrm{C\vdots C}.$$

This expression equals—

$$2(n+1-a-2b-p)(\mathrm{C}/4+\mathrm{H}+\mathrm{C.H})\\+(n+p-a-b-1)(\mathrm{C}/2+\mathrm{C.C})+a(\mathrm{C}+\mathrm{C{:}C})+b(\tfrac{3}{2}\mathrm{C}+\mathrm{C\vdots C}).$$

Now, put $W=\mathrm{C}/4+\mathrm{H}+\mathrm{C.H}$, $X=\mathrm{C}/2+\mathrm{C.C}$, $Y=\mathrm{C}+\mathrm{C{:}C}$, $Z=\tfrac{3}{2}\mathrm{C}+\mathrm{C\vdots C}$, the original expression then becomes—

$$2(n+1-n-2b-p)W+(n+p-a-b-1)X+aY+bZ.$$

From this identity two conclusions follow:—

1. From adequate data the values of W, X, Y, and Z can be calculated, but not those of C, H, C.H, C.C, C:C, and C $\vdots$ C, because the value of any and every hydrocarbon can be expressed in terms of W, X, Y, and Z; hence only four different equations can be obtained even if the values of every hydrocarbon were known, and four equations involving six unknowns are indeterminate.

2. The coefficients of W, X, Y, and Z are respectively identical with those of C.H, C.C, C:C, and C $\vdots$ C; hence although we cannot obtain the true values of C.H, C.C, C:C, and C $\vdots$ C, if we calculate these on the assumption that C and H are both nil, the values obtained will hold for all purposes of calculating results and verifying formulæ. *In other words, the physico-chemical property of any hydrocarbon (and, as I have already indicated, the argument can be extended to other classes of compounds) is completely determined by the number and sort of valency-bonds its molecules contain, the value of the property in question being the sum of a series of products obtained by*

multiplying the number of each sort of bond by a quantity varying according to the bond, but always constant for the same bond. Now, the quantity which must be multiplied by the number of, say, (M.M′) bonds, may be suitably written f(M.M′), and may be defined as the effect on the physico-chemical property in question determined by the presence in its molecule of one M.M′ bond. We may then write—

$$nC+2(n+1-a-2b-p)H+2(n+1-a-2b-p)C.H+(n+p-a-b-1)C.C+aC{:}C+bC\vdots C\equiv 2(n+1-a-2b-p)f(C.H)+(n+p-a-b-1)f(C.C)+af(C{:}C)+bf(C\vdots C).$$

Instead of the letter f, different letters may be employed to distinguish one property from another.

The validity of the foregoing will, perhaps, become even more apparent if some actual examples of the implied method of calculation are given. There is an enormous amount of data to which the method is applicable, but the labour involved in collecting these data, tabulating them, and eliminating doubtful results is immense. I propose to restrict myself to data which have already been collected, giving only a few typical specimens of the method of calculation and results.

1. *Molecular Weight.*

As a matter of considerable theoretical interest I venture to point out again what I showed in the article in *Knowledge* already referred to, that the method is applicable to the calculation of molecular weights (or, as they should preferably be called, molecular inertiæ). If w(M.M′) is the "inertia equivalent" of any energy complex M.M′, *i.e.*, the effect on, or contribution towards, the molecular weight of a body of the bond M.M′, the total molecular weight being regarded as due to the bonds, then—

$$w(M.M') = n\left(\frac{m}{v}+\frac{m'}{v'}\right),$$

where m, m' are the atomic weights of the elements M, M′, v, v' their valencies, and n the number of bonds involved. Thus, if the atomic weights of C, H, and O are taken as 12, 1, and 16 respectively—

$$w(C.C) = 1\left(\frac{12}{4}+\frac{12}{4}\right) = 6$$

$$w(C{:}C) = 2\left(\frac{12}{4}+\frac{12}{4}\right) = 12$$

$$w(C\vdots C) = 3\left(\frac{12}{4}+\frac{12}{4}\right) = 18$$

$$w(C.H) = 1\left(\frac{12}{4}+\frac{1}{1}\right) = 4$$

$$w(C.O) = 1\left(\frac{12}{4}+\frac{16}{2}\right) = 11$$

$$w(C{:}O) = 2\left(\frac{12}{4}+\frac{16}{2}\right) = 22$$

$$w(O.H) = 1\left(\frac{16}{2}+\frac{1}{1}\right) = 9$$

It will be found that the molecular weight of any C, H, and O compound calculated by means of these constants is exactly the same as that calculated from the atomic weights C = 12, H = 1, O = 16, as the reader may readily verify for himself for, say, the compounds given in Table I., or any others containing these three elements, thus:—

Mol. wt. of ethyl alcohol = m(C.C)+5m(C.H)+m(C.O)+m(O.H) = 6+5×4+11+9 = 46.

Mol. wt. of dimethyl ether = 6m(C.H)+2m(C.O) = 6×4+2×11 = 46, &c.

The method can, of course, be extended to other classes of compounds, containing other elements.

2. *Molecular Heat of Combustion.*

Source of Data.—I shall use Thomsen's results corrected for constant volume, collected in my "On the Calculation of Thermo-chemical Constants," confining my attention to fatty hydrocarbons and certain of their oxygen derivatives.

Notation.—q(C.H), q(C.C), &c. It will be understood that q(C.H), for instance, is not the value in thermic units of the C.H link—which value, as proved above and in the former paper in *Knowledge* already referred to, cannot be calculated at the present state of knowledge—but the effect on heat of combustion determined by the presence in each molecule of the body by one C.H bond. Similar remarks hold for the other constants.

The values of the constants for bonds between C, H, and O may be calculated thus:—

M.H.C. of methane, (CH_4) = 210·8 cals.
∴ 4q(C.H) = 210·8 cals., ∴ q(C.H) = 52·7 cals.

M.H.C. of ethane, (C_2H_6) = 369·0 cals.
∴ 6q(C.H)+q(C.C) = 369·0 cals., ∴ q(C.C) = 52·8 cals.

Mean result for all suitable chain hydrocarbons investigated by Thomsen = 52·9 cals.

M.H.C. of ethylene, (C_2H_4) = 332·2 cals.
∴ 4q(C.H)+q(C:C) = 332·2 cals., ∴ q(C:C) = 121·4 cals.

Mean result = 121·8 cals.

M.H.C. of acetylene, (C_2H_2) = 309·2 cals.
∴ 2q(C.H)+q($C\vdots C$) = 309·2 cals., ∴ q($C\vdots C$) = 203·8 cals.

Mean result = 203·8 cals.

M.H.C. of dimethyl ether, ($CH_3.O.CH_3$) = 348·2 cals.
∴ 6q(C.H)+2q(C.O) = 348·2 cals., ∴ q(C.O) = 16·0 cals.

Mean result = 15·0 cals.

M.H.C. of carbon dioxide, (CO_2) = nil.
∴ q(C.O) = nil.

M.H.C. of water, (H_2O) = nil.
∴ q(O.H) = nil. (*a*)

(*a*) This is only on the assumption that the two O.H bonds in water are equal, against which I have brought forward certain evidence ("On the Calculation of Thermo-chemical Constants," § 13).

Using these values, namely, q(C.H) = 52·7 cals., q(C.C) = 52·9 cals., q(C:C) = 121·8 cals., q($C\vdots C$) = 203·2 cals., q(C.O) = 15·0 cals., q(C:O) = nil, the molecular heats of combustion of over two dozen bodies have been calculated, and are compared with the experimental results in Table I. The method can be used, with entirely similar results, in the case of molecular heats of formation.

3. *Molecular Refractivity.*

Source of Data.—Molecular refractivity is calculated from the refractive index by means of various formulæ, of which that of Lorentz-Lorenz is to be preferred. I shall only deal with the aliphatic hydrocarbons here, using values for refractivities for the Hα line calculated from the experimental results of Landolt and Jahn, Perkin, and Brühl, collected in a paper "On the Calculation of Optico-Chemical Constants," by myself, published in the CHEMICAL NEWS in 1910 (vol. cii., pp. 3 6 and 14—15).

Notation.—r(C.H), r(C.C). &c. The values of the constants can be calculated in a somewhat similar manner as in the case of heat of combustion constants, or derived from my former optico-chemical constants. The mean values are as under:—

r(C.H) = 1·74, r(C.C) = 1·09, r(C:C) = 4·04

(The value of r($C\vdots C$) is uncertain owing to lack of data).

Some results, using these constants, are shown in Table II. The results are about twice as accurate as those obtained by Brühl's method.

TABLE I.—*Molecular Heat of Combustion.*

Body.	Ordinary formula.	Valency-bond formula.	M.H.C. Experimental. Cals.	M.H.C. Calculated. Cals.	Error. Cals.
Methane	CH_4	$(C.H)_4$	210·8	210·8	±0·0
Ethane	C_2H_6	$(C.H)_6(C.C)$	369·0	369·1	+0·1
Propane	C_3H_8	$(C.H)_8(C.C)_2$	527·5	527·4	−0·1
Trimethylmethane ..	C_4H_{10}	$(C.H)_{10}(C.C)_3$	685·2	685·7	+0·5
Tetramethylmethane ..	C_5H_{12}	$(C.H)_{12}(C.C)_4$	844·8	844·0	−0·8
Di *iso*propyl	C_6H_{14}	$(C.H)_{14}(C.C)_5$	996·6	1002·3	+5·7
Ethylene	C_2H_4	$(C.H)_4(C:C)$	332·2	332·6	+0·4
Propylene	C_3H_6	$(C.H)_6(C.C)(C:C)$	491·3	490·9	−0·4
iso-Butylene	C_4H_8	$(C.H)_8(C.C)_2(C:C)$	648·9	649·2	+0·3
iso-Amylene	C_5H_{10}	$(C.H)_{10}(C.C)_3(C:C)$	805·6	807·5	+1·9
Diallyl	C_6H_{10}	$(C.H)_{10}(C.C)_3(C:C)_2$	930·8	929·3	−1·5
Acetylene	C_2H_2	$(C.H)_2(C \vdots C)$	309·2	308·6	−0·6
Allylene	C_3H_4	$(C.H)_4(C.C)(C \vdots C)$	466·4	466·9	+0·5
Dipropargyl	C_6H_6	$(C.H)_6(C.C)_3(C \vdots C)_2$	881·4	881·3	−0·1
Dimethyl ether	C_2H_6O	$(C.H)_6(C.O)_2$	348·2	346·2	−2·0
Methyl ethyl ether ..	C_3H_8O	$(C.H)_8(C.C)(C.O)_2$	504·4	504·5	+0·1
Diethyl ether	$C_4H_{10}O$	$(C.H)_{10}(C.C)_2(C.O)_2$	657·9	662·8	+4·9
Methyl allyl ether ..	C_4H_8O	$(C.H)_8(C.C)(C:C)(C.O)_2$	625·7	626·3	+0·6
Diallyl ether	$C_6H_{10}O$	$(C.H)_{10}(C.C)_2(C:C)_2(C.O)_2$	909·4	906·4	−3·0
Methyl propargyl ether	C_4H_6O	$(C.H)_6(C.C)(C \vdots C)(C.O)_2$	602·7	602·3	−0·4
Methylal	$C_3H_8O_2$	$(C.H)_8(C.O)_4$	474·9	481·6	+6·7
Methyl formate	$C_2H_4O_2$	$(C.H)_4(C:O)(C.O)_2$	240·6	240·8	+0·2
Methyl acetate	$C_3H_6O_2$	$(C.H)_6(C.C)(C:O)(C.O)_2$	398·4	399·1	+0·7
Methyl propionate ..	$C_4H_8O_2$	$(C.H)_8(C.C)_2(C:O)(C.O)_2$	552·8	557·4	+4·6
Methyl *iso*-butyrate ..	$C_5H_{10}O_2$	$(C.H)_{10}(C.C)_3(C:O)(C.O)_2$	715·5	715·7	+0·2
Ethyl formate	$C_3H_6O_2$	$(C.H)_6(C.C)(C:O)(C.O)_2$	339·2	339·1	−0·1
Propyl formate	$C_4H_8O_2$	$(C.H)_8(C.C)_2(C:O)(C.O)_2$	557·6	557·4	−0·2
iso-Butyl formate ..	$C_5H_{10}O_2$	$(C.H)_{10}(C.C)_3(C:C)(C.O)_2$	718·4	715·7	−2·7
Allyl formate	$C_4H_6O_2$	$(C.H)_6(C.C)(C:C)(C:O)(C.O)_2$	527·0	520·9	−6·1
Acetic anhydride ..	$C_4H_6O_3$	$(C.H)_6(C.C)_2(C:O)_2(C.O)_2$	459·5	452·0	−7·5

TABLE II.—*Molecular Refractivity.*

Body.	Ordinary formula.	Valency-bond formula.	Mα. Experimental.	Mα. Calculated.	Error.
Pentane	C_5H_{12}	$(C.H)_{12}(C.C)_4$	25·30	25·24	−0·06
Hexane	C_6H_{14}	$(C.H)_{14}(C.C)_5$	29·70	29·81	+0·11
Heptane	C_7H_{16}	$(C.H)_{16}(C.C)_6$	34·32	34·38	+0·06
Octane	C_8H_{18}	$(C.H)_{18}(C.C)_7$	38·95	38·95	±0·00
Decane	$C_{10}H_{22}$	$(C.H)_{22}(C.C)_9$	48·21	48·09	−0·12
Amylene	C_5H_{10}	$(C.H)_{10}(C.C)_3(C:C)$	24·65	24·71	+0·06
Hexylene	C_6H_{12}	$(C.H)_{12}(C.C)_4(C:C)$	29·34	29·28	−0·06
Octylene	C_8H_{16}	$(C.H)_{16}(C.C)_6(C.C)$	38·55	38·42	−0·13
Decylene	$C_{10}H_{20}$	$(C.H)_{20}(C.C)_8(C:C)$	47·38	47·56	+0·18
Valerylene	C_5H_8	$(C.H)_8(C.C)_2(C:C)_2$	24·16	24·18	+0·02
Diallyl	C_6H_{10}	$(C.H)_{10}(C.C)_3(C:C)_2$	28·77	28·75	−0·02

TABLE III.—*Molecular Volume.*

Body.	Ordinary formula.	Valency-bond formula.	M.V. Experimental.	M.V. Calculated.	Error.
Butane	C_4H_{10}	$(C.H)_{10}(C.C)_3$	95·9	95·6	−0·3
Pentane	C_5H_{12}	$(C.H)_{12}(C.C)_4$	117·8	118·0	+0·2
Hexane	C_6H_{14}	$(C.H)_{14}(C.C)_5$	139·9	140·4	+0·5
Heptane	C_7H_{16}	$(C.H)_{16}(C.C)_6$	162·6	162·8	+0·2
Octane	C_8H_{18}	$(C.H)_{18}(C.C)_7$	186·3	185·2	−1·1
Amylene	C_5H_{10}	$(C.H)_{10}(C.C)_3(C:C)$	109·9	110·7	+0·8
Hexylene	C_6H_{12}	$(C.H)_{12}(C.C)_4(C:C)$	132·4	133·1	+0·7
Heptylene	C_7H_{14}	$(C.H)_{14}(C.C)_5(C:C)$	154·6	155·5	+0·9
Octylene	C_8H_{16}	$(C.H)_{16}(C.C)_6(C:C)$	177·6	177·9	+0·3
Valerylene	C_5H_8	$(C.H)_8(C.C)_2(C:C)_2$	104·5	103·4	−1·1
Diallyl	C_6H_{10}	$(C.H)_{10}(C.C)_3(C:C)_2$	125·8	125·8	±0·0

4. *Molecular Dispersion.*

The molecular dispersion of a body is the difference between its molecular refractivities for the $H\alpha$ and the $H\gamma$ lines. In the paper already referred to I have shown that the effects on molecular dispersion of the C and H atoms, as well as the C.H bond, are negligible, whereas those of C.C and C:C bonds are 0·13 and 0·32 respectively.

5. *Molecular Volume.*

Source of Data.—The term "molecular volume" is here used to denote the product of molecular weight and the reciprocal of specific gravity. Some values for the fatty hydrocarbons at their boiling-points are here given, taken from a paper by Mr. Gervaise Le Bas, published in the CHEMICAL NEWS for 1908 (vol. xcviii, pp. 85—86), where they are used to support a different hypothesis.

Notation.—$v(\text{C.H})$, $v(\text{C.C})$, &c. The values of the constants have been calculated in a way somewhat similar to that adopted in the case of the former constants, and are found to be as under:—

$$v(\text{C.H}) = 7{\cdot}1,\quad v(\text{C.C}) = 8{\cdot}2,\quad v(\text{C:C}) = 15{\cdot}1.$$

(No data are here given from which to calculate the value of $v(\text{C} \vdots \text{C})$).

The tabulated results (see Table III.) show an excellent agreement between the calculated and experimental values.

To sum up: it is evident from the foregoing results that many important properties of bodies can be regarded as primarily functions of the number and sort of valency-bonds within their molecules. This has been shown to be true of the most characteristically atomic property, namely, molecular weight, and, within an adequate degree of accuracy, of certain other properties, and it has been proved mathematically that any property which can be attributed to, or treated as a function of, the number and sort of atoms composing the molecules of a body can *ipso facto* be attributed to, or treated as a function of, the number and sort of valency-bonds which may also be said to compose the molecules of that body. Thus, so it seems to me, another link has been forged in the chain of evidence for the view that matter is an energy-phenomenon—its different forms being different manifestations of energy, the product, so to speak, of different energy-complexes.

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FEEDING A NATION.*

By Prof. D. NOEL PATON, M.D., F.R.S.,
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The main object of the lecture is to show that feeding a nation should depend upon a knowledge of the dietary requirements of the population as determined by scientific observation and experiment, and that any attempt to regulate the food supply which is not directly based upon such knowledge is more likely to do harm than good.

The fundamental fact is that *food is the sole source of energy, of the power of doing work.*

The food requirements of the nation is the sum of the food requirements of the constituent individuals which varies with their ages, sex, and occupation.

The energy expended by a man while at rest and while doing different amounts of work has been accurately measured, and these measurements have been checked by the examination of the diets of men under different conditions. The general result arrived at is that a man doing moderate work should take food at least 3400 energy units (*calories*) per day.

The requirements of women and of children of different ages are estimated as definite fractions of those of a man doing moderate work.

The Nation's Food Supply in Pre war Time.

By applying the above data to the census returns for 1911, it is found that the whole population was equivalent to nearly 35 million "men," and it is thus evident that the nation required a minimum supply of 43½ million million calories of energy in the food consumed in the year.

This energy is yielded by the three great constituents of the food, the proteins, fats, and carbohydrates; and experience has shown that in European countries these are taken in something like the proportions—proteins, 100 grms.; fats, 100 grms.; and carbohydrates 500 grms. per man per day.

A study of the food supply of the nation shows that in pre-war time a considerable excess was consumed. The figures are—proteins, 113 grms.; fats, 130 grms.; carbohydrates, 571 grms.; calories, 4009.

An investigation of the diets of the labouring classes shows that the food supply was unequally distributed, and that these classes were getting on an average a little over 3000 calories per "man" per day, indicating that waste among the more well to do classes must have been excessive.

The foodstuffs from which these energy yielding constituents were derived are cereals which yielded nearly 35 per cent of the energy, meat about 17 per cent, dairy produce about 15 per cent, potatoes about 8 per cent, while all other foodstuffs made up the remaining 12 per cent of energy.

The prime importance of cereals, whether eaten directly by human beings as bread-stuffs, or indirectly after being converted by live-stock into meat, milk, &c., is thus demonstrated. The unfortunate fact that 80 per cent of our wheat, far and away the most important of these cereals, is imported has to be recognised.

The Nation's Food Supply in War Time.

The requirements of the nation have been modified by the increase in the military and naval establishments, and by the increased call for work from the civil population.

Evidence has been adduced that up to the end of 1916 the food supply remained not less than in pre-war time, and this being the case it is found that after making the necessary deductions for the fighting forces an adequate allowance was still available for the civil population as a whole.

But the increase in prices has somewhat accentuated the inequality of distribution. Dietary studies of the labouring classes show that while generally the increase of income has kept pace with the increased cost of living, those whose incomes have not increased have suffered real hardship.

The Part which the State should Play in Feeding a Nation in War Time.

The part which the State should play in feeding a nation in war time is:—First, to secure an adequate supply of food; second, to secure an equitable distribution of the supply.

The prime importance of the supply of bread-stuffs as human food dominates the situation. This supply may be maintained or increased (1) by increased importation, (2) by better milling, (3) by limiting their use as cattle food, (4) by limiting their use in brewing and distilling. Increased production at home is a policy of the future.

To secure equitable distribution various courses, separately or combined, are possible:—(1) To raise wages proportionately to the rise in the price of food; (2) while doing this, in the case of the organised trades, at the same time to make provision for those whose wages are not increased by supplying bread to them at a lower price; (3) to limit the rise of prices by fixing maximum prices; (4) to limit price by decreasing consumption.

A consideration of these seems to point to the conclusion that the best course is to allow the natural rise of prices by which supply is stimulated and waste checked, but to make provision for the supply of bread-stuffs and possibly of other foods at a price proportionate to their income to those whose wages have not risen proportionately to the rise in prices.

Detection of Iron in Filter-paper Purified with Hydrofluoric Acid.—Gawalowski (*Zeit. Anal. Chem.*, through *Mining and Engineering Review*).—The iron in imperfectly washed filter papers has been found to be present mainly as a cellulose compound (ferrous cellulosate), and not as free oxide. On acidifying with hydrochloric acid or sulphuric acid and treating with potassium thiocyanate a red colour results after oxidation by the air.—*Chemical Engineering and the Works Chemist*, vii., No. 73.

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* Abstract of lecture delivered at the Royal Institution of Public Health, July 11, 1917.

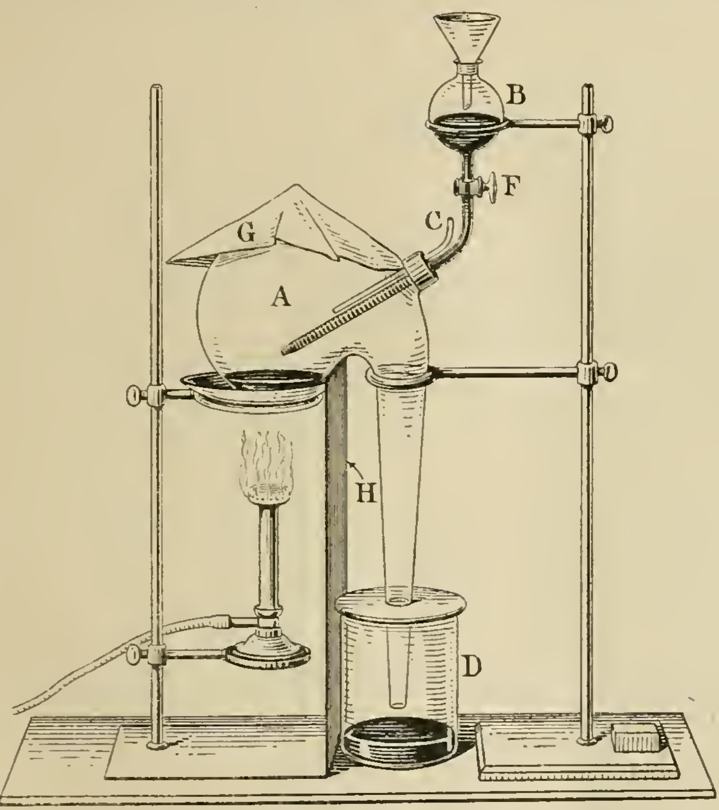
A SIMPLE METHOD FOR THE PURIFICATION OF MERCURY.

By HORACE BARRATT DUNNICLIFFE.

The method described in this article was used for the purification of about half a hundredweight of mercury and was found to yield the mercury in a sufficiently high state of purity to give no tails or surface blemishes even after six months. The greater part of the mercury was used for filling barometers and electric meters, and very dirty mercury was submitted for cleaning. It is essential that the surface of mercury used in electric meters should be perfectly clean, otherwise the meters run slow and record a lower consumption than is actually used.

At first I used the methods of fitering through leather, shaking with sugar, cleaning with nitric acid in the usual way, and then washing with distilled water and drying.

Several samples of "purified" mercury cleaned in this way were returned as unsatisfactory, and it was stated that, on standing, the surface became contaminated. I then decided that the mercury purified by the above method must be distilled from glass. I had no means of getting the usual forms of apparatus and finally used the apparatus shown in the figure, which has several advantages, not the least of which are the simplicity of its construction and ease in manipulation. It is now six months since I submitted the first sample cleaned by the method and no complaints have been received from those using the purified mercury.



All parts of the apparatus and all vessels used are specially cleaned by (1) caustic soda, (2) acids and bichromate mixture, and then washed with distilled water and dried by a current of hot air which has been carefully dried and scrubbed free from all suspended matter. Open vessels were sometimes dried by washing with alcohol and then ether.

The apparatus consists essentially of an ordinary retort A, through the tubulure of which passes the stem of a dropping funnel B, bent as shown, and also a piece of ordinary glass tubing C.

The tubes are packed in place by means of asbestos. The retort is placed as shown and pressed into a bath consisting of a mixture of sand and iron filings. During the heating the iron oxidises and forms a solid bed for the retort. The neck of the retort points downwards and passes through a perforated glass coverslip into a small glass beaker D. E is a sheet of asbestos board (H) to protect the neck of the retort from over-heating. G is asbestos paper placed over the bulb of the retort to prevent loss of heat by radiation.

Care must be taken to fasten all parts of the apparatus properly. Some mercury is run into the retort and the Fletcher burner lighted. The mercury distils over quietly and without bumping and condenses in the upper part of the neck of the retort. There it collects into globules which run into the beaker. Mercury is poured into the funnel B by means of the conical funnel, and the tap F is easily adjusted so that mercury drips into the retort at about the same rate as it drops into the beaker.

The mercury distils at the rate of about an ounce in four minutes. During the distillation the inside of the retort became dirty with a blackish mass which represented the oxidised impurities. The distillate was redistilled, but a very small portion of the surface appeared dull. This slight impurity can be completely removed, when it occurs, by pouring the mercury into a dropping funnel. Shake the funnel and allow the mercury to stand a few minutes and then run the mercury *slowly* out of the funnel. The small quantity of impurity which had apparently been carried over by the mercury vapour is left in the narrow neck of the dropping funnel as the last few drops of mercury leave it. The mercury is run directly into specially cleansed bottles and stoppered.

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THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.[*]

PART I.—SOLIDS.

By IRVING LANGMUIR.

THE importance of the work of W. H. Bragg and W. L. Bragg in its bearing on chemistry has not, as yet, been generally recognised. In hearing two of W. H. Bragg's lectures in this country a few years ago, the writer was impressed with the very great significance of this work in the field of chemistry. The structure of crystals as found by the Braggs leads to new and more definite conceptions as to the nature of chemical forces.

The writer has constantly endeavoured to apply this new conception in his work on heterogeneous reactions, and particularly in connection with a study of the phenomena of adsorption and surface tension. In this way he has gradually been led to form more or less definite theories of the mechanism of evaporation, condensation, liquefaction, adsorption, and capillary phenomena. According to this theory, both solids and liquids consist of atoms held together entirely by *chemical forces*. The conception of the molecule thus almost entirely loses its significance except in the case of gases. In fact, we may well look upon any solid or liquid body as constituting a single large molecule. Any change of phase, such as the melting of a solid, is thus a typical chemical reaction. The mobility of liquids, according to this viewpoint, is due to a kind of tautomerism.

The present paper is merely an outline of this theory. The more detailed description of the experimental work upon which it is largely based, will be reserved for future papers.

Structure of Crystals.

The idea that a crystal should constitute an effective diffraction grating for X-rays originated with Laue (*Sitzb. d. Bayer. Akad. d. Wiss.*, June, 1912), who also saw that by means of such a grating not only could the wave-length of the X-rays be determined, but also a powerful method for studying the structure of crystals was made available. The detailed theory developed by Laue proved incorrect in certain important respects. W. L. Bragg called attention to these errors, and gave a theory by which the true structure could be determined from the diffraction pattern. (*Proc. Camb. Phil. Soc.*, 1912, xvii., 43; the subsequent papers of W. H. and W. L. Bragg were published in 1913 and 1914 in the *Proc. Camb. Phil. Soc.*, the *Proc. Roy. Soc.*, and the *Phil. Mag.*; all of these papers were translated into German and were published together in one volume of the *Z. Anorg. Chem.*, 1914, xc.) Since then the method has been greatly simplified, so that at present it is usually a matter of no great difficulty to find the exact arrangement of the atoms in a crystal. In this way the structures of some 30 or more kinds of crystals have been determined.

The alkali halides NaCl, KCl, KBr, and KI all have a similar structure in which the *atoms* are arranged according to a simple cubic lattice. Thus, in the case of sodium chloride crystals, sodium and chlorine atoms alternate along three sets of lines at right angles to each other. Each sodium atom is surrounded by six equidistant chlorine atoms arranged around it, as the corners of an octahedron are arranged around its centre. Similarly, each chlorine atom is surrounded by six equidistant sodium atoms.

Up to this time it had been taken for granted that crystals were built up of molecules. But from this work of the Braggs it is clear that in crystals of this type the identity of the molecules is wholly lost, except in so far as we may look upon the whole crystal as composing a single molecule. From the arrangement of the atoms we must conclude that the forces holding the crystal together (cohesion) are forces which exist directly between sodium and chlorine atoms. Every chemist looks upon such forces as chemical in nature. (Of course, all chemical forces are probably of electromagnetic origin, but for this reason we do not need to call the forces in crystals by the vague term "physical forces," and thus distinguish them from chemical force).

But the significance of this structure for the chemist extends further. Sodium is invariably regarded as a monovalent element, yet in the sodium chloride crystals we see a structure which in no wise suggests the monovalent character of the atom. The sodium atom is held by chemical forces to six chlorine atoms. If we retain the conception of valency in such a case, we must clearly admit that the valency of the sodium is divided equally between the six chlorine atoms.

If a sodium chloride crystal evaporates at high temperature, the atoms leave the surface in pairs in the form of sodium chloride molecules. These molecules are formed in the process of evaporation, since they do not exist as such in the crystal. The process of evaporation is thus a chemical process.

In the diamond, each carbon atom is surrounded by four others equidistant from it. These are arranged around the central one in the same way as the four corners of a regular tetrahedron are arranged around its centre. In this case the tetravalent character of the carbon atom manifests itself clearly. When a model of a diamond crystal is examined, it is seen that the atoms appear to be arranged in rings of six, corresponding to the benzene ring. The remarkable strength of the carbon chain and especially the stability of the benzene ring, so familiar to chemists, is thus seen to be the cause of the hardness, the high melting point, and the low vapour pressure of the diamond.

It is interesting to note that the structure of zinc blende, ZnS, is very similar to that of the diamond, the zinc and sulphur being alternately substituted for adjacent carbon atoms. Thus each zinc atom is surrounded by four symmetrically placed sulphur atoms, while each sulphur atom is surrounded by four zinc atoms. The valency is thus again divided.

With fluorite, CaF_2, each fluorine atom is surrounded by four symmetrically placed calcium atoms, while each calcium atom has eight fluorine atoms arranged around it like the eight corners of a cube about the centre of the cube.

The structure of pyrites, FeS_2, is much more complicated. Each iron atom has four equidistant sulphur atoms around it, but there are other sulphur atoms at distances only slightly greater. Similarly, each sulphur atom has three equidistant iron atoms forming a triangle around it, but above and below the plane of this triangle there are other iron atoms whose distance is only slightly greater.

Hauerite, MnS_2, has a similar structure to that of pyrites.

In the case of calcite, $CaCO_3$, the carbon and oxygen atoms lie in planes perpendicular to the crystal axis. Three oxygen atoms are arranged in groups around each carbon atom, forming an equilateral triangle. The calcium atoms lie in planes just above and just below the carbon-oxygen planes. Each calcium atom has six equidistant oxygen atoms around it. The distance between the calcium and the carbon atoms is considerably more than either the distance between oxygen and carbon, or between oxygen and calcium. Thus the crystal is evidently held together by forces acting between carbon and oxygen and between oxygen and calcium. The group CO_3 appears as a unit, since each carbon atom is associated with three oxygen atoms, while these are associated with only the one carbon atom. But each CO_3 group is equidistant from six calcium atoms, so that it is impossible to pick out any one of these as forming a molecule with the CO_3. If we are to retain the idea of a molecule at all, we must consider that the entire crystal is a single molecule.

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[*] From the *Journal of the American Chemical Society*, xxxviii., No. 11.

In dolomite, $CaMgCO_3$, the structure is exactly similar, except that calcium and magnesium planes alternate. The structures of rhodochrosite, $MnCO_3$, siderite, $FeCO_3$, and sodium nitrate, $NaNO_3$, are like that of calcite. This last case is of special interest to the chemist, since a monovalent atom replaces a divalent, and a pentavalent (?) atom replaces a tetravalent one without causing a change in the arrangement of the atoms.

The crystals of magnetite afford an illustration of a structure in which different atoms of the same element have different functions. Two-thirds of the iron atoms occur in positions in which each is surrounded by four oxygen atoms (tetrahedral arrangement), while the other third of the iron atoms are each surrounded by six oxygen atoms. The iron atoms have thus a divalent and trivalent character, but each unit of valence is divided between two oxygen atoms. Spinel, $MgAl_2O_4$, has an exactly similar structure in which the Mg atoms take the place of the divalent iron atoms, while the Al atoms replace the trivalent iron atoms.

Crystals of metallic copper and metallic silver have been found to have their atoms arranged according to the face-centered cubic lattice. This arrangement is the same as the familiar one obtained when round shot are piled in layers as regularly and compactly as possible. In this structure each atom is equidistant from the twelve adjacent atoms.

The structures of crystals of rhombic sulphur and quartz have been partly worked out. In the sulphur crystals the atoms are found to be arranged in a lattice structure in groups of eight. The particular arrangement of the atoms within these groups is not yet known. To the chemist it is of significance that these groups of eight contain the same number of atoms as are found in molecules of sulphur vapour. Here, then, for the first time, the crystal has a structure in which the identity of the molecules (as found in the gas phase) is apparently not wholly lost.

In a recent article (*Phil. Mag.*, 1916, xxxii., 65) L. Vegard shows that the structures of gold and lead crystals are the same as those of silver and copper. He also describes the structure of the zircon group of minerals represented by zircon, $ZrSiO_4$, rutile, TiO_2, and cassiterite, SnO_2. The structure of zircon proves to be especially interesting, for it is found "that each of the Zr or Si atoms is associated with two oxygen atoms; thus the groups SiO_2 and ZrO_2 form a kind of 'molecular elements' of the lattice. This is not merely a way of regarding the geometrical arrangement of the atoms; but we have reason to believe that the groups SiO_2 and ZrO_2 form chemically saturated compounds" within the crystal.

Two facts stand out clearly as a result of the consideration of these crystal structures. In the first place, it is evident that crystals are built up of atoms in such a way that each atom is chemically combined to all the adjacent atoms, while these in turn are combined to those beyond.

Secondly, we see that the arrangement of the atoms in general does not follow the usual rules of valency, but that each atom is combined with a much larger number of atoms than corresponds to its normal valence.

In the past it has been customary to consider that solids and liquids are held together by the "forces of cohesion" and to call these "physical forces" as distinguished from chemical forces. Often these distinctions are known to be rather vague, but in the more recent years, with growing confidence in the atomic theory, we have been accustomed to consider that chemical phenomena are those involving an alteration of the structure of molecules, while physical phenomena are those in which only the molecule as a whole is concerned. This distinction throws the whole difficulty back on to the definition of the molecule. In gases there is usually no uncertainty as to the size of the molecules, but in liquids and solids no really satisfactory methods have been found for determining molecular weights. As long as we cannot definitely determine the molecular weights, it thus remains impossible to distinguish sharply between chemical and physical phenomena. Nevertheless, much discussion has arisen of late years over such questions as whether adsorption and surface tension are chemical or physical phenomena. The overwhelming consensus of opinion seems to be that these are both physical phenomena.

In the following pages the writer hopes to show that there is no present justification for this distinction between chemical and physical forces. Cohesion, adsorption, and surface tension are all manifestations of forces similar in their nature to those acting between the atoms of solid bodies. It is therefore advantageous to look upon these forces as direct results of chemical affinity. In this way it becomes possible to correlate these so-called physical phenomena with the known chemical characteristics of the atoms and groups of atoms forming the bodies.

(To be continued).

A KINETIC HYPOTHESIS TO EXPLAIN THE FUNCTION OF ELECTRONS IN THE CHEMICAL COMBINATION OF ATOMS.*

By WILLIAM A. NOYES,
Department of Chemistry, University of Illinois.

Beginning with Davy (1) and Berzelius, during the first part of the nineteenth century chemists generally accepted the theory that chemical combination is due to electrical forces, but when Dumas discovered the chloroacetic acids in which chlorine atoms, supposedly negative, replace positive hydrogen atoms it was believed that the theory had been shown to be false, and it was practically abandoned. Following this, for fifty years or more, a theory of valence which took no account of electrical forces was developed, and while occasional reference was made to positive and negative atoms and groups, no definite meaning in an electrical sense was attached to these expressions. Helmholtz in his Faraday lecture in 1881 (2) drew the attention of chemists once more to the very close connection between chemical forces and electrical phenomena, and spoke for the first time of "atoms of electricity." He also pointed out that the "sulphur of sulphuric acid must be charged with positive equivalents of electricity." In 1887 Arrhenius proposed his theory of electrolytic dissociation, and with the help of Ostwald and van 't Hoff the belief in a separation of molecules into electrically charged parts in solutions was rapidly accepted. J. J. Thomson (3) gave precision to the atomic character of electricity in 1897 when he demonstrated the material character of cathode rays and the very minute mass of the corpuscles carrying negative charges. Van 't Hoff (4) seems to have suggested for the first time that electrically charged atoms may play a part in reactions not usually considered as ionic. The same idea was proposed by the author (5) and by Stieglitz (6), a little later. J. J. Thomson (7) seems to have been the first to suggest that two atoms may be held together by the electrical forces resulting from the transfer of an electron from one to the other. He assumed a shell of electrically positive matter within which there was a static arrangement of electrons. Abegg (8) in an entirely independent paper published the same year, discussed the relation between electrons and ionisation, and the connection with older theories of Helmholtz and others. He also raises, I think for the first time, the question of polar and non-polar valences, but seems to have decided that the former are more probable (9). Rutherford (10) has advanced strong reasons for considering that atoms contain a positive nucleus around which electrons are rotating, and this hypothesis has been further developed by Bohr, (11), Nicholson (12), Moseley (13), and others.

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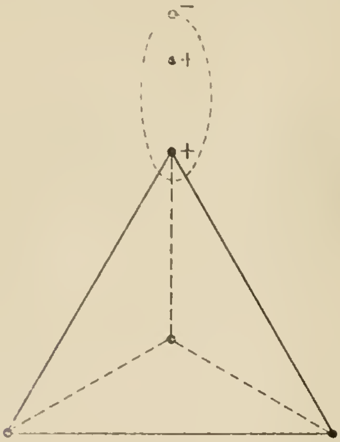
* Read before the National Academy of Sciences, U.S.A., April 16, 1917. From the *Proceedings of the National Academy of Sciences*, iii., No. 5.

Physicists, in general, have directed their attention to rotating or rapidly moving electrons, and to the relation between these and spectral lines, the disintegration of atoms and other phenomena involving individual atoms. Chemists, on the other hand, following the suggestion of J. J. Thomson, have considered chiefly the *rôle* which the valence electrons probably play in the combination of atoms. Sir William Ramsay (14) in his Address on "The Electron as an Element" considered that the electron takes a position between the two atoms which are held in combination. In a very recent paper, probably the last which he wrote (15), he elaborates this thought further, and describes models to illustrate the magnetic attractions which would result from electrons rotating in contiguous parts of two molecules. The magneton theory of the structure of the atom has also been developed elaborately by Parson (16). It cannot account for ionisation, where, if we accept the electron theory at all, electrons must be transferred completely from the positive atom or group to the negative. Falk and Nelson (17), Fry (18), L. W. Jones (19), Stieglitz (20), Bray and Branch (21), G. N. Lewis (22), and others have discussed the phenomena connected with the transfer of valence electrons from one atom to another, but, with the exception of the magneton theories referred to above, no one, so far as I can discover, has suggested a possible connection between the motion of the valence electrons and chemical combination between atoms.



In the hypotheses here proposed the following assumptions, now more or less current among physicists and chemists, are made:—

1. The atoms are of a complex structure made up of positive nuclei and electrons, of which the latter at least are in very rapid motion. If we assume that the electrons are 1/1800 the mass of hydrogen atoms and that they obey the same laws of motion as other atoms, their average velocity would be about sixty times the velocity of molecules of hydrogen (H_2). I will not attempt to discuss here the question whether the law of equipartition of energy actually holds for electrons.

2. That the electrons are of two kinds in their relation to the structure of the atom. Some of them are so involved in their orbits or motions among the positive nuclei that they can never escape from the atom. Others, called valence electrons, may be transferred to other atoms.

Let us suppose that two atoms, which have an affinity for each other, are brought close together. A valence electron which is rotating around a positive nucleus in the first atom may find a positive nucleus in the second atom sufficiently close so that it will include the latter in its orbit, and it may then continue to describe an orbit about the positive nuclei of the two atoms. During that portion of the orbit within the second atom that atom would become, on the whole, negative, while the first atom would be positive. During the other part of the orbit each atom would be electrically neutral, and the atoms might fall apart. When we remember, however, the tremendous velocity of the electrons and the relatively sluggish motions of the atoms it seems evident that the motion of an electron in such an orbit might hold two atoms together. In ionisation the electron would, of course, revolve about the nucleus of the negative atom leaving the other atom positive. It seems impossible to explain ionisation otherwise than on the supposition of the complete transfer of the electron. This complete transfer in ionisation is one of the strongest arguments against the magneton theory as the only explanation of chemical combination.

An interesting feature of the hypothesis proposed is that it may be used to account for the localisation of the affinities in particular parts of atoms which is indicated by many of the properties of organic compounds. Thus if we suppose that there are four (or eight) positive nuclei in a carbon atom around which valence electrons may rotate, an atom of hydrogen may be held to the neighbourhood of one of these nuclei as indicated in the figure.

I wish to acknowledge my indebtedness to Julius Stieglitz, R. D. Carmichael, J. B. Shaw, Jacob Kunz, A. P. Carman, A. A. Noyes, and R. C. Tolman, who have read the first draft of this paper and of whom several have made helpful suggestions.

Notes.

(1) Davy, *Phil. Trans.*, 1807, p. 1.

(2) Helmholtz, *Journ. Chem. Soc.*, 1881, xxiv., 291.

(3) J. J. Thomson, *Phil. Mag.* (Ser. 5), 1897, xliv., 291.

(4) Van 't Hoff, *Ibid.*, 1901, xxiii., 797.

(5) W. A. Noyes, *Journ. Am. Chem. Soc.*, 1901, xxiii., 463.

(6) Stieglitz, *Ibid.*, 1901, xxiii., 797.

(7) J. J. Thomson, *Phil. Mag.*, (Series 6), 1904, vii., 237.

(8) Abegg, *Zeit. Anorg. Chem.*, 1904, xxxix., 330.

(9) *Loc. cit.*, Note 8, p. 347.

(10) E. Rutherford, *Phil. Mag.* (Series 6), 1911, xxi., 669.

(11) N. Bohr, *Ibid.*, 1913, xxvi., 1, 476, 857. On p. 862 Bohr discusses the hypothesis that atoms may be held in combination by electrons rotating about the line joining the positive nuclei of two atoms. This is similar to Ramsay's view mentioned below.

(12) Nicholson, *Phil. Mag.* (Ser. 6), 1914, xxvii., 54.

(13) Moseley, *Ibid.*, 1913, xxvi., 1024.

(14) Sir W. Ramsay, *Journ. Chem. Soc.*, 1908, xciii., 774.

(15) Sir W. Ramsay, *Proc. Roy. Soc.*, A, 1916, xcii., 451.

(16) Parson, "A Magneton Theory of the Structure of the Atom," *Smithsonian Inst., Misc. Collect.*, 1915, lxv., No. 11.

(17) Falk and Nelson, *Sch. Mines. Q.*, Columbia Univ., 1909, xxx., 179; *Journ. Am. Chem. Soc.*, 1910, xxxii., 1637.

(18) Fry, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 1268; *Zeit. Phys. Chem.*, 1911, lxxvi., 385, 398, 591.

(19) L. W. Jones, *Journ. Am. Chem.*, 1914, xxxvi., 1268.

(20) Stieglitz, *Ibid.*, 1914, xxxvi., 272; 1916, xxxviii., 2046.

(21) Bray and Branch, *Ibid.*, 1915, xxxv., 1440.

(22) G. N. Lewis, *Ibid.*, 1915, xxxv., 1448.

EXPERIMENTAL FARMING IN COUNTY DURHAM.

The following articles, descriptive of a visit paid on 5th June, 1917, to Prospect House Farm, Bolam, by a party of Press representatives in company with Mr. Frank P. Walker, M.Sc., Adviser in Agriculture, Armstrong College, Newcastle, and Mr. Laidlaw, sub-commissioner appointed by the Board of Agriculture, are reprinted from the *Auckland and County Chronicle*:—

The value of the true wild white clover as an aid of almost incalculable character in the reclamation of pasture and meadow land was emphasised very strongly during an inspection by a party of Press representatives at Prospect House Farm, Bolam, in the occupation of Mr. T. G. Robinson, a prominent agriculturist, and one who has done a great amount of good in carrying out experiments during the last few years. The visit was arranged by Mr. Frank P. Walker, M.Sc., Adviser in Agriculture, Armstrong College, Newcastle, and accompanying the party was Mr. Laidlaw, one of the sub-commissioners appointed by the Board of Agriculture, and himself a farmer with many years' experimental experience.

A Pressing Need.

The pressing need to-day, if the food problem is to be satisfactorily overcome, and the menace of the submarines broken down, is for British agriculturists to be given all the encouragement possible by the Government, and for farmers, individually and collectively, to plough out as much pasture and meadow land as they can possibly spare for the growing of wheat, barley, and oats, and other cereals.

A good deal of unnecessary anxiety has arisen in the minds of farmers with regard to the breaking up of rich pasture lands, a prevailing idea being that the land cannot be reclaimed for pasture purposes under ten years. How mistaken this idea is can be seen in the experiments which are being conducted on many farms in the county of Durham under Mr. Walker's able guidance. There has, of course, been a certain amount of prejudice shown by the more old-fashioned farmers to the scientific methods of agriculture, but Prospect House Farm, at Bolam, stands to-day a glowing testimony to the value of science as applied to agriculture. Throughout the visit the Press representatives received the greatest courtesy from Mr. Robinson, his mother, and sister, who display managerial ability very much above the ordinary. The visit gave many lasting impressions.

On Leggs Across Farm.

We first visited a 15 acre field on the Leggs Across Farm, where we began to make our comparisons. Twelve years ago this field was full of whins or gorse. When Mr. Walker commenced his experiments he divided this field into three plots, one of six acres, another of five, and a third of four acres, and his primary object was to note the results from the application of different mixtures supplied by different merchants. Mr. Robinson, acting upon advice tendered to him, purchased a certain mixture, and into this incorporated one pound of the true wild white clover seed per acre. In the two other portions of the field the clover seed was sown to the extent of 3 lb. per acre, the object here being to quickly get what is called the sole. It must be borne in mind that in 1914 this field was in barley and wheat. Late in 1914 the young seeds were top dressed with basic slag containing the equivalent to total phosphates in 10 cwt. per acre of high quality slag. The results in the form of hay crops in the years 1915-16 were eminently successful, and this year it is again going to be hay. The scheme of manuring in this field was an extremely simple one. After the wheat and barley were cut in 1914, the field was very closely grazed with stock and manured with high quality basic slag, which was supplied about Christmas. After examining the result achieved in the three portions, the conclusion was very obvious that ordinary arable land can be put down to permanent pasture of a good character in two or three years' time with economic and sound results. The land will be ploughed out in the autumn of this year, and oats will be grown in 1918.

On other parts of the farm similar experiments are being carried out, and land which is being used for pasture and meadow purposes has been ploughed out and is being put through the course of cropping. It will be laid away in due course with mixtures similar to those in this 15 acre field, and with the same object in view.

An Objection Met.

One of the objections which farmers still make to ploughing out pasture land in order to assist the country in its time of need and stress by growing food is that they would not then have sufficient land to carry their stock. As a matter of fact, Mr. Robinson's farm is carrying more stock and producing more milk every day. Because during the whole of these experiments the arable land is being improved out of all recognition, and at the same time the experiments are improving the permanent grass and meadows.

During our inspection of this field we discussed the prices of seed, which is always one of some importance to the farmer, because very many farmers are loth to spend excessive sums of money unless they can be absolutely assured beyond all question of doubt that the results are going to compensate them to the full for this expenditure. It is unfortunate, of course, but the increase in the price of clover seed is due to economic conditions—that the supply is not equal to the demand. Originally 1s. to 1s. 6d. per lb. when the experiments began in 1906, the price rose until in 1916 it reached a guinea, and to-day it is 8s. 6d. to 10s. per lb. This high price is undoubtedly militating against the work of the agricultural experts, and at a time when farmers need to be encouraged to the fullest extent to carry out the advice tendered.

Value of True Wild White Clover.

The value of incorporating the true wild white clover is distinctly shown when a field such as the one we described is treated differently. The farmer in this case will get an indirect benefit, because when that field is ploughed out next year with oats, he will get six to eight bushels per acre more than in the other portions, and that is entirely due to the clover root. The chief thing, of course, is to get a plentiful supply of the clover, and farmers can do it for themselves if they will only take the trouble to grow it. Before leaving this field we were struck with the wonderfully thick sole produced by mixtures similar to those used at Cockle Park. The small amount of wild white clover sown extra in the top portion had spread very rapidly and was very thick, but there was no comparison between the sole of the two pastures. The dividing line in the three portions of the field was distinctly seen.

Passing on to a second field of 30 acres, the experiment took the form of having the grass very closely grazed and then taking the stock out and allowing the clover to form seeds. With regard to the phosphates used in the manuring of this field, Mr. Walker said that of one thing he was absolutely certain, and that was what is mainly lacking in our British soil are phosphates of lime and lime. We were constantly taking them away and not bringing them back in proper proportion.

The object of the experiment in this second field was to test the capabilities of the phosphates—in low and high citric solubility slags. The phosphates in some low quality slags are practically insoluble, while in other low quality slags they are soluble in a two per cent solution of citric acid.

In November, 1914, Mr. Walker stepped out two half acres of this field of four riggs straight up the field, and Mr. Robinson put down a ton per acre of low citric soluble slag on one portion, and the same weight of low grade slag with a high citric solubility guarantee on the adjoining area. He appealed to the Press representatives to express their opinion as to the different treatment, and it was generally agreed that although it was more economical in the long run to buy high grade slag, yet the results justified the encouragement to use basic slag, whether of high or low grade citric solubility, even if of low quality, in order that farmers might improve their pasture and meadow land.

Prospect House Farm occupies a very commanding position. Looking away to the South there is a splendid view of all the country surrounding Piercebridge, and to the right the pretty old-world village of Ingleton, with its red tiled roofs, is another conspicuous landmark. At the time that a number of Press representatives visited the farm to see for themselves the results of recent experiments the day was one of brilliant sunshine, and although the land was badly in need of rain the general prospects for the autumn looked exceedingly good.

It should be pointed out that Mr. Walker has been able to do this work, reference to which was made in a first article which appeared in the *Chronicle* last week, through the grant which the Durham County Council has made to Armstrong College, Newcastle-on-Tyne, and the Agricultural Department of that college appreciates very much the great amount of interest which the County Council have for some years displayed in agriculture.

One of Many.

High Prospect Farm is only one of quite a number of farms in the county and in the North of England where Mr. Walker's guidance and expert knowledge are being made use of, and it is hoped that in the course of the next few weeks he and others interested in the experiments will make visits to some of those farms and note the results of experiments under varying conditions of soil, &c.

In the article published last week dealing with High Prospect Farm experiments reference was made to the wonderful results which had accrued from the use of the true wild white clover seed as an energiser, and the experiments with seed mixtures containing this clover seed. We further referred to results that have been achieved from the use of high and low citric solubility slags on pasture land. And the results also on recently ploughed out land with cereals properly manured and otherwise cultivated are extremely good.

The value of these experiments will be appreciated by farmers more fully when it is recognised that this farm of 400 acres in area is a scattered one. The high lying fields are quite 500 feet above sea level, the soil is variable in character, but a good deal of it is of a heavy, brashy character, not too well drained, and typical of the boulder soils of the district. Although it directly overlooks the fertile valley of the Tees, the nature of the soils and the prevailing climatic conditions make it quite a fortnight to a month later than the warmer soils and the more favourable climate of the lower-lying Tees Valley lands. At the time of our visit Mr. Robinson explained that he was quite three weeks later in his work than some of the farmers not five miles away, so that the very varied character of climatic conditions is something which has to be counted upon quite seriously.

Some Contrasts.

The task of giving in detail the numerous points which were raised and discussed during this full day's inspection would occupy a very considerable amount of newspaper space, and as that space at the present moment is seriously limited we are obliged in this second article to sum up the remainder of the day's inspection as briefly as is consistent with a clear acknowledgment of the great value of the experimental work which Mr. Walker has carried out in conjunction with Mr. Robinson.

The tour of the southern portion of the farm, after luncheon, took us into about half a dozen fields, some of which had been pasture for a great many years. They were now ploughed out, and carrying either cereals or potatoes. There was abundant evidence from the large areas of land which had been treated with Cockle Park and other mixtures that wild white clover seed properly fed was a virile, healthy renovator of failing seed mixtures which had been laid away without its incorporation.

One field which has second year seeds upon it produced in 1916 about 3 tons 12 cwt. of hay per acre. In 1915 this field was in oats, but unfortunately the oats grubbed off, and Mr. Walker decided that the remaining crop should be grazed by sheep, and afterwards that the maiden seeds should be dressed with 10 cwts. per acre of high quality slag. In 1916, as already referred to, it gave one of the biggest crops of clover he had ever seen.

Adjoining this field, to the north, was what has been an old pasture field of 14 acres laid away some twenty years ago, and in speaking about the renovating value of the wild white clover seed Mr. Walker, in one of his eulogistic outbursts, described it as "a soul-inspiring plant."

A Divided Field.

In other fields we visited were noted the very satisfactory results of wheat and straw crops, and on the return journey to the farm we noticed a 20-acre field which was laid away at great expense and trouble in 1908. As so frequently happens, every particle of clover had died away in a very short time, and the result was a very poor, harsh, dry pasture. The experiment, with a view to renovating this land, took the form of dividing the field up into four plots, one of which was manured with 10 cwt. per acre of high quality slag; No. 2 with a slightly different mixture; and plots 3 and 4 were heavily harrowed in May, 1914, and a renovating seed mixture containing wild white clover seed was sown, with the same dressing of slag plus 6 cwt. of kainit per acre. In 1915 on a re-seeded portion they had had very fine results as compared with the slagged though not re seeded portions. Even the most casual glance over the field showed the striking effect of the wild white clover seed.

Before leaving the farm the Press representatives made a tour of the farm buildings. Here, as in every other part of the farm, were to be found the same evidences of careful management and skill. The working of the farm, however, is very largely in the hands of Mrs. Robinson and her daughter, who have the assistance of a number of farm hands. We reached the farm just about milking time and were able to witness the milking operations conducted on the very latest scientific principle of milking by machinery. The farm is very heavily stocked, and al the stock appear to be in first-class condition.

Before bidding adieu to Mr. and Mrs. Robinson and Miss Robinson, the Press representatives expressed their delight and pleasure at having the privilege of making so close an acquaintance with High Prospect Farm, and wished the tenants an even greater measure of success in the coming season.

Institute of Chemistry.—*Pass List, July* (1917) *Examinations.*—The results of the Examinations of the Institute of Chemistry recently held in London, Dublin, and Johannesburg have now been published. Four candidates passed the Intermediate Examination, viz., E. R. Baines; (Miss) Ella Caird; W. H. Craven, B.Sc. (Lond.); and A. J. Dando. Four candidates passed the Final (A.I.C.) Examination, viz., H. J. Hegan, B.Sc. (Lond.), in Mineral Chemistry; A. J. Hall, B.Sc. (Lond.), and S. J. Rogers, B.Sc. (Lond.), in Organic Chemistry; and H. Jephcott, B.Sc. (Lond.), in the Chemistry (and Microscopy) of Food and Drugs, Fertilisers, and Feeding Stuffs, Soils, and Water. Two candidates passed the Final Examination for the Fellowship, viz., H. R. Adam, B.Sc. (Aberd.), in Metallurgical Chemistry; and George Taylor, in the Chemistry of Food and Drugs, &c.

CORRESPONDENCE.

RE NEW ELEMENT.

To the Editor of the Chemical News.

Sir,—I notice in the Chemical News of June 15 (cxv., 288) Mr. Lister, replying to my notes describing an element which I believe to be new, suggests that the element in question is europium. This element is placed in the yttrium group of rare earths precipitated by oxalic acid. It will be noted that the element I have described gives no precipitate with that reagent.

The analysis of the sulphate clearly proves that it is not europium—

1. By heating a known weight of the anhydrous sulphate to redness the following result was obtained :—

Sulphuric anhydride	55·80 per cent
Oxide	44·20 per cent
	100·00

2. By dissolving a known weight of anhydrous sulphate in water, adding a slight excess of caustic potash, and filtering, the filtrate, after adding hydrochloric acid and boiling, is treated with chloride of barium.

The following result was obtained :—

Sulphuric anhydride	55·07 per cent
Oxide	44·93 per cent
	100·00

The probabilities are that the atomic weight of this element is less than half that of europium. I might add that the anhydrous sulphate absorbs water very quickly when exposed to the air, and becomes quite liquid in a few hours.—I am, &c.,

W. Bramley.

Middlesbro'.

AGRICULTURAL EDUCATION.

To the Editor of the Chemical News.

Sir,—Twenty-one years ago as an English student at Edinburgh University I made a solemn vow that The God (of Christ) helping me, instead of going back to farm work I would henceforth work in the interests of Agricultural Education through the farmer on behalf of the farmer. To the best of my ability that vow has been honourably kept. It is not that I have a "penchant" for the farmer as a farmer, but merely because I long ago recognised that agriculture (in its broadest sense) is the most important, noblest, and essential industry to any country.

It grieves me intensely to think that nothing less than a World War has been necessary to demonstrate the truth of my convictions.

Because of my vow in 1896 in many English counties and South Africa it has been my fortune to suffer in health, wealth, reputation, and social position. Fortunately, since I ceased to worry about the inefficiency of officials who were my superiors in office, my health has been completely restored. And work, work, work well done I have long since realised as man's greatest blessing and source of true happiness. The three last factors I do not care twopence about.

Ten years ago I was appointed Lecturer in Agriculture at Armstrong College, Newcastle-upon-Tyne. So far as county work is concerned my work as Lecturer and Adviser in Agriculture has been mainly in County Durham, through Northumberland, Westmoreland, Cumberland, and North Yorkshire farms, and farmers have had my services in a less degree.

My life-history is an open one to all whom its concerns. For years inefficient officialdom has prevented me disclosing many important truths as to the possibilities of Agriculture in the British Isles. The main reason has been because, recognising as I do and have done that we must be governed, it has been necessary to control myself and not to go behind those in authority to get my way, which all along I have known in accordance with results obtained, was right.

In February last my services were requisitioned as Executive Officer to the Durham County War Agricultural Executive Committee. As a result, so far as this appointment (of quite an honorary character) is concerned I am a free man, and do not by disloyalty to anybody dishonour myself in writing to you.

With the help of thousands of progressive farmers, pitmen, and the industrial population I am convinced that it is possible for these "Tight Little Islands" to feed, *and* in quick time, their teeming populations. But only under certain conditions.

Through my many progressive farmer friends I have for years increased the production of food-stuffs immensely *and economically* on thousands of acres of land, good, bad, and indifferent.

The North Country Press has helped me to do this most magnificently. What I want now is the help of the Pres of the whole country. The enclosed particulars of a 400 acre farm which has been improved beyond recognition during the past five years are only a fraction of what can be done, and what has been done on farms in the North of England. In due course, it is my intention, all being well, to let you have further particulars of other farms with distinct, true, and independent evidence of what has been and is possible to be accomplished on our island farms with an economic combination of labour, capital, and brains.

The *principal conditions* which must be granted and prevail, if the British Isles are to be made quickly and profitably self-supporting are as follows :—

1. Greater and ever greater efforts must be put forth immediately by the Government and the farmers themselves to provide skilled farm labourers (both men and women), horses, motor tractors, manures, &c., for increased grain and stock production.

2. Now and in the future agriculture must not be made a political shuttlecock between contending parties.

3. Our present landowners must take greater personal interest in their tenantry and farm workers, as distinct from leaving so much control to bootlicking (in so far as men above them socially are concerned) and tyrannical so-called land agents (in so far as men below them socially are concerned). Amongst these agents are thousands of men of true nobility of character, and who have a sound knowledge of farming. These men I love and revere. As for the incompetents amongst them "the least said soonest mended."

4. The Press, which I have always recognised as truly and nobly having done its best work in the interests of our race and empire, must now and in the future do its very utmost to establish (and teach the populace) the true importance of Agriculture in these Islands. On the other hand, there is, in my opinion, no needs for "ists" and "isms" in this inspiring theme.

5. Now and in the future the pitmen and our industrial population must, through their powerful organisations, as they will for a very long time remain in the majority, "see to it" that our essential industry "Agriculture" is never again sacrificed for the interests of "Industrialism"; as it has been sacrificed in past generations. Some of my greatest friends are pitmen and workmen, and I have such unbounden faith in their sense of "Justice" that when once the question of the importance of "Agriculture" is put to them, without class prejudice, they will do what millions of our race and I want them to do, viz., support, help,

and encourage "Agriculture" in our British Island Homes.

6. While all this is being done *we* must *educate, educate, educate*. And in this way *not* pull down but *lift up and up*. I am absolutely certain that when every member of our race pays more attention to "Duties as distinct from Rights," the true ideals for which the Anglo-Saxon race and her noble allies are fighting will be the sooner attained.

7. In connection with "Education." We ourselves must in future pay more attention to the fact that "Education" and "Scholarship" are not synonymous terms. And my ideal of a truly educated man (used in the generic sense) is the one who gives of his best, no matter what may be his birth, breeding, or social position, for the welfare, uplifting, and happiness of his fellow men.

I trust you will not think me troublesome in writing at such great length. For I well know what great sacrifices you as editors have to make during these strenuous but soul-uplifting times. But (while I fully realise that the sword of true "Justice" loving Democracy must conquer the sword of "Injustice" loving Prussian Autocracy) in spite of everything "The pen is mightier than the sword." For the latter killeth while the former maketh alive.

I trust you also will acquit me of egoism or desire for advertisement, as this letter is written really in a spirit of great humility. Neither do I want you to take my work and aspirations at my own valuation.

Therefore if you have any doubts as to the wisdom of doing so, please send one of your best agricultural correspondents to make a tour with me or self-respecting agriculturists of many districts, and see what, with the help of my colleagues and hundreds of good, sound, progressive farmers, I have done during the past ten years in increasing food production on farms in counties Durham, Northumberland, Westmoreland, North Yorkshire, &c.

You are at liberty to make whatever use you like of this letter and accompanying inclosures.

In conclusion, I wish to express my gratitude to my Executive Committee, of which Mr. H. G. Stobart, Witton Towers, Witton-le-Wear, is chairman. This committee is composed of a truly honourable body of men, progressive farmers, landowners, and agents. They are working hard and with true self-sacrifice in our Imperial interests. To them I owe the freedom which has enabled me to write this letter and do many other things for the furtherance of agriculture without the slightest feeling of disloyalty to any one.—I am, &c.,

Frank P. Walker, Adviser in Agriculture, Executive Officer to the Durham War Agricultural Executive Committee.

P.S.—Do please try to realise that in spite of my remarks about "inefficients" that I bear these men not the slightest personal ill-feeling. According to their lights they have done their best. But for years their lights have been exceeding dim. Nothing except what I personally conceive to be in the true interest of our race and Empire would have induced me to write as I do and have done. In future "Efficiency" must take the place of "Inefficiency" with all "our powers that be," if as a governing and world controlling race we are to hold our own and progress.—F. P. W.

NOTES AND QUERIES.

_ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Metallic Calcium.—Can any correspondent inform me where I can obtain information as to the manufacture or extraction of pure calcium, and if such a process could be undertaken by one person.—F. M.

TO comply with Regulation 8 (b) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

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THE CHEMICAL NEWS.

Vol. CXVI., No. 3010.

THE CHINESE STUDENT OF CHEMISTRY.

By FRANK BROWNE, F.I.C.

The Chinese readily take to the study of chemistry, particularly to the practical side. At first it is astonishing how ignorant they are of the most elementary operations, such as filtration and the use of test-tubes. But after being once shown they seldom require further attention in such matters. The Chinese students of whom experience is to be recorded, were attending evening classes at the Hongkong Technical Institute. During the day they were occupied mostly as shop assistants and as clerks. Before enrolment all were required to show a knowledge of English subjects, sufficient to justify tuition. The fees were very low, and did not nearly cover the expense to the Government. After several trials during two or three years, it was found that the teaching found to be most suitable was to take a text-book, such as the second volume of "Elementary Practical Chemistry," by Clowes and Coleman (translations in Chinese are on sale in book shops), and to proceed so that at the end of the first year the students had a thorough knowledge of the chart for the separation of the ordinary metals. Then almost every student could detect easily and quickly any one of these, when given in solution, together with a common acid. They were able also to recognise by physical appearance most of the commonly occurring inorganic compounds. No attempt was made during the first year to teach them more than this. The identification of the metals and their salts was found to be much liked by the native. There is no doubt that a great deal can be learned from such apparently simple analyses. An early training of this kind, which prevents a pupil from jumping to conclusions, which teaches him to make a proper deduction from the results of his experiments, and to think logically, and withal maintaining his interest in the subject, cannot be regarded otherwise than as a good method of instruction. Two evenings weekly were devoted to practical chemistry, and the students were advised to attend a class in theoretical also, but this they were not always able to do. But, somehow or other, these students would so apply themselves to the writing and understanding of equations, that at the end of the first year they were able to write a full account of their work when examining inorganic substances. Seeing that at the commencement of the course such words as sodium, magnesium, and the like, were absolutely without significance to these learners, the progress indicated was deemed to be satisfactory. Several students showed excellent ability after several years training, and could grasp without difficulty anything taught them. One in particular became devoted to chemistry. With the aid of some useful books that he had purchased, he prepared to get out an encyclopædia of chemistry. Thus, under "Antimony," he had written down all his own observations, together with an epitome of the sections in his books relating to this metal. He was advised to stop this, as it entailed a burden of work in collecting particulars that could be as well studied in a good text-book. Nothing, however, could prevent this student from getting out a chart for the metals, which was a masterpiece of its kind, containing on one large sheet all the separations and special tests, with other observations. This was printed at his own expense, and its study seemed to be a source of unfailing interest to himself and to many of his fellow-students.

It is not intended here to weary the reader with details as to the course followed. The tuition was strictly individual, and the work to be done became increasingly difficult for each year of study. At the end of the third year a student who had passed the set examinations in theoretical and practical chemistry, mathematics, and physics could obtain a diploma, which was much prized. But students could, and did, continue their studies, taking up those methods of analysis which seemed most likely to be helpful.

Hongkong is full of small industries of the most diverse kind, and among them are native white-lead, tanning, distilling (liquor), soap-making, glass-blowing, canning, boat-building, and metallurgical works. Then there is an enormous demand for toilet articles, many of which are put up locally by those with sufficient knowledge and skill to suit the taste of the Chinese public. Local manufacturers are greatly assisted by the use of duty-free alcohol. Thus in the bean curd canning industry, alcohol may be denatured with salt. In perfumery, the spirit is no longer dutiable after the addition of a small quantity of oil of neroli, lavender, or of any suitable substance approved by the Government. Students that have attended the Technical Institute readily understand such matters, and soon make use of their knowledge for business purposes.

At first it was a difficult matter to get students to sit for examinations. They did not like to fail, which means much more to them than to Europeans. However, by means of monthly tests, it was possible to get them to look at the matter in another light, but it may be said generally that a Chinese does not at all like to go in for an examination unless fully expecting to pass.

From time to time good hard-working students would announce their intention of leaving for Europe. In case of a youth likely to succeed, it is sometimes customary in China for his relatives to club together so that he may receive a first-class European training. This is regarded as a very good investment. It may be said, in short, that whatever the case may be in other countries, in China nothing pays so well as money spent on education. In the European settlements, with only a secondary school training, the son of a coolie cannot fail to obtain a well-paid situation, in which he can easily repay the amount advanced for his training. The Chinese who go to Europe do not consider their studies finished for practical purposes when they have taken a degree. Frequently they leave one seat of learning to undergo special training at others. Here it may be pointed out that Chinese students regard with little favour teachers, lecturers, and the like, who cannot teach. These latter may be very learned, but unless possessing the quality indicated, their lectures will be but sparsely attended. Nothing is so likely to ruin a college as to have a teaching staff largely composed of lecturers with little aptitude for imparting to others their own knowledge.

The Chinese, in brief, are capable of being taught science. They have a natural taste for anything practical. As is well known, in business they are very successful, and there is no reason why, in the future, in the industrial applications of science, they should not be able to apply modern methods to their numerous industries, and to make use of Western training for developing the natural resources of their country. This opening up of China is surely, even if apparently but slowly, coming, and the good work which has been, and is being, done by the various European teaching institutions in the East will be of immense service in bringing to this industrious, peace-loving nation some of the advantages bestowed invariably on those showing a genuine devotion to the acquirement of knowledge and to the practice of science.

Scientific Research in France. — The French Académie des Sciences en France have decided to establish a National Physical and Mechanical Laboratory for the purpose of scientific research, directed in a marked degree to the benefit and use of the industries. Existing laboratories engaged in similar work will be affiliated to the National Laboratory, and will work in close relationship to the latter.

MATTER AND ELECTRICAL PHENOMENA.

By F. H. LORING.

I NOTE Mr. H. Stanley Redgrove's letter in the CHEMICAL NEWS, cxv., 204. With your kind permission I should like to submit the following notes and comments:—

(1) Light, which in general is emitted by matter, is an electromagnetic disturbance, or radiation of electrical origin.—Maxwell Hertz.

(2) The atom is known to be *partly* electric, or electronic in structure.—J. J. Thomson, Lorentz, Rutherford, and others.

(3) Matter may be wholly "electric" if the counterpart to negative electricity (electrons) is matter itself, but conferring on matter the electric title does not in this case mean that it is endowed with the characteristics belonging to the electron. The duality may comprise matter pure and simple on the one hand, and the negative electrons on the other.—See statement by Soddy below.

(4) Valency is systematically altered (in the case of the radio-elements) concurrently with the emission of alpha particles (positively charged helium atoms), and beta rays (negative electrons).—Soddy, Russell, Fajans, and others.

(5) The "essential mechanism of all chemical reaction is . . . to be sought in the action of light [radiation] upon atoms."—Perrin, "Atoms," 163 (trans. by Hammick, pub. by Constable and Co.).

(6) Gravitational attraction may be of electromagnetic origin.—See CHEMICAL NEWS, cxv., 181. See also Einstein's hypothesis of gravitation based upon the relativity theory, which seemingly accounts for the observed secular motion of the nodes of the planet Mercury, the actual value being 43' of arc per century: the calculated value being 42·9'.

(7) An electrified body possesses an electrical inertia, or electromagnetic mass, apart from its mechanical mass, except in the case of an electron, which is supposed to have electromagnetic mass only.—J. J. Thomson.

(8) A magnetised body may possess magnetic inertia.—See Walker's paper, abstract in CHEMICAL NEWS, cxv., 201.

(9) The force of attraction between masses of matter may undergo a slight variation with temperature (this requires further confirmation).—See Shaw's experiment.

(10) The theory of relativity, which has sprung up in electromagnetic soil, when applied to ponderable matter indicates that *mechanical mass* should obey the laws of *electromagnetic mass*.—See (13).

(11) The quantum theory involves the assumption that the Newtonian laws (classical mechanics) fail when applied to radiation phenomena, including the photo electric effect.—See Jean's "Report on Radiation and the Quantum Theory," and also, by the same author, "The Dynamical Theory of Gases," second edition, p. 398 onwards. In this connection see Perrin's statement (5), especially with regard to the photo-electric effect.

(12) In certain radio-atomic explosions, the negative electrons are expelled with a velocity approximating to that of light, and their electromagnetic mass has been observed to vary in accordance with the relativity theory.—Kaufmann and others.

(13) It has been assumed from relativity considerations that *all* mass is electromagnetic.—See Bumstead, *Am. J. Sci.*, 1908, xxvi., 493.

(14) "The electron theory of matter," based upon many experiments, is sufficiently comprehensive to overrule purely mechanical considerations when evaluating the relations of matter to electricity.

The above facts and theories may lead one to suppose that all matter is purely electric or electromagnetic in character, and, in consequence, the Newtonian laws do not apply either to cases involving very high mass velocities, or to the dynamics of electric systems.

My contention is that when matter is considered in the Newtonian sense the Newtonian laws apply, and that any phenomenon specifically involving—

(*a*) The æther, assuming its existence, or

(*b*) Negative electrons, or

(*c*) Radiation, which is an electromagnetic disturbance or propagation, does not come within the orthodox view of matter, and therefore the scrapping of the Newtonian laws is not justified, or at least until more is known.

Therefore, so far as ponderable matter is mechanically concerned, it makes no difference, in my opinion, whether one refers to a *mass* of 1 gm., or 1 gm. *quantity of matter*, or the *inertia* of 1 gm., and by cancelling the unit term the equivalence will be apparent.

Matter may be defined provisionally as a body which, owing to its self-contained state, obeys the Newtonian laws, in distinguishment from that which is not matter by reason of its failure to obey the Newtonian laws.

The tendency of modern science is to co-ordinate the above-mentioned phenomena under a monistic doctrine, so to speak. Even if such a doctrine proves wrong, it may be conducive to great strides in the development and application of science.

The following statement attributed to Prof. Soddy, in *Engineering*, of May 25, 1917, being a report of his Royal Institution discourse, is of interest in this connection: "The confusion between the earlier and present views concerning the relations between matter and electricity," Prof. Soddy continued, "was a further obstacle to the student. We knew negative electricity apart from matter as the electron; we knew positive electricity, apart from the electron, the hydrogen atom or the alpha particle (helium atom), and that was matter in the electrically uncombined condition. Whether we spoke of positive and negative electricity, or matter and electricity, the dualism remained. On the other hand, the theory of electromagnetic inertia was true monism; it tried to explain two things, the inertia of the electron and the inertia of matter, by the same cause. There was no reason to assume that matter minus its electron was made of the same stuff as the electron itself."

Mr. Redgrove's idea that *inertia* is a *property*—see Note—and that it should be applied to matter so as to leave it (matter) undefined as such, has a great deal in its favour, as will be seen from the above statements (1, 2, 3, &c.), but even so, in mechanics some word is necessary which implies a material substance. Mr. Redgrove, however, argues that, for reasons already stated, the Newtonian laws should be abandoned. I agree that they may be thrown overboard ultimately, to use Mr. Redgrove's simile, but are we not justified in still regarding electrical phenomena, or negative electricity itself, as a sort of complement to matter proper, requiring, therefore, a complementary law, or set of laws, distinct from those of Newton?

(NOTE.—A *property* may be an acquired attribute, or one not invariably of fixed value. In contradistinction, a sphere *is* round, or mass *is* matter in the Newtonian sense. Crabb ("English Synonyms," 1916: Harper's) says: "We may give or take away *properties* from bodies at pleasure, without entirely destroying their identity." *Property* also denotes a peculiar quality or that which is inherent to the thing or concept involved, and it was in this sense that I referred to the electrical phenomena simulating matter in respect of inertia).

In referring to the relativity and quantum theories, it should be understood that the phenomena and experiments which form the basis of these theories are to be considered from the points of view necessarily taken as being incompatible with the Newtonian laws, *i.e.*, with the classical mechanics. Moreover, the quantum theory is in direct conflict with the wave theory of light, *i.e.*, with the undulatory theory. Mr. Redgrove is, of course, conversant with these matters, but the general reader may not be aware of the conflict between certain departments of science—if I may so express it.

STUDIES OF THE CARBONATES.*

Hydrolysis of Sodium Carbonate and Bicarbonate and the Ionisation Constants of Carbonic Acid.

By CLARENCE ARTHUR SEYLER
and
PERCY VIVIAN LLOYD.

The ionisation constant of carbonic acid in the equilibrium equation $[H] \times [HCO_3] = k_2 [H_2CO_3]$ is well established by the experiments of Walker and Cormack, and has the value $3\cdot04 \times 10^{-7}$ at 18°.

The value of the second ionisation constant in the equation $[H] \times [CO_3] = k_3 [HCO_3]$ is, however, still uncertain, even after correction of the value deduced by Bodländer (*Zeit. Phys. Chem.*, 1900, xxxv., 32), from the experiments of Shields (*Ibid.*, 1893, xii., 167), which was first made by McCoy (*Am. Chem. Journ.*, 1903, xxix., 437).

This is due to the fact that the value of k_3 found experimentally varies with the concentration of the carbonate.

Two methods have been used, namely:—

1. That of McCoy (*loc. cit.*), who determined the ratio—

$$\frac{k_2}{k_3} = \frac{[HCO_3]^2}{[CO_3]\,[H_2CO_3]}.$$

2. That used by Shields (*loc. cit.*), who determined the ratio—

$$\frac{k_w}{k_3} = \frac{[HCO_3]}{[CO_3]}.[OH],$$

by experiments on the hydrolysis of ethyl acetate, and by Auerbach and Pick (*Arb. Kais. Gesundheitsamt*, 1911, xxxviii., 11), who determined the hydrogen concentration colorimetrically. In both cases the values of $\frac{k_2}{k_3}$ and $\frac{k_w}{k_3}$ increase decidedly with dilution, but not in the same ratio, as would be expected if k_3 were really subject to variation. This can scarcely be the case, so that the cause of the apparent variation must be sought in the degree of ionisation of the carbonate and bicarbonate.

Let k_c be the apparent value of the ratio—

$$\frac{C_{NaHCO_3}}{C_{Na_2CO_3}.[H_2CO_3]}$$

and k_d of the ratio—

$$\frac{C_{NaHCO_3}}{C_{Na_2CO_3}}.[OH].$$

The values of $[H_2CO_3]$ and $[OH]$ do not involve any ionisation correction, the latter having been directly determined either by the hydrolysis of ethyl acetate or by a colorimetric method; but the values of C_{NaHCO_3} and $C_{Na_2CO_3}$ require to be multiplied by the degree of ionisation of the respective salts α and β. Hence—

$$(1)\ \frac{k_2}{k_3} = k_c \frac{\alpha^2}{\beta} \text{ and } (2)\ \frac{k_w}{k_3} = k_d \frac{\alpha}{\beta};$$

From this it is evident that k_c and k_d will not increase proportionately.

Attempts have been made by all workers to form estimates of the value of α and β. Stieglitz (*Carnegie Inst. Publication*, No. 107) assumes the dissociation of sodium bicarbonate to be the same as that of sodium acetate. This is probably a fair approximation. The ionisation of the carbonate has been assumed to be the same as that of sodium sulphate. This is more doubtful. Stieglitz assumes for a concentration of 100×10^{-3} $\beta = 0\cdot687$ and for 300×10^{-3} $\beta = 0\cdot584$. These are no doubt too high, since Harkins and Bray show (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1864) that ions such as $NaSO_4$ exist in concentrated solutions. Bray estimates for $c = 100 \times 10^{-3}$ $\beta = 0\cdot598$ and for $c = 1000 \times 10^{-3}$ $\beta = 0\cdot420$. Auerbach and Pick simply assume a value $\beta = 0\cdot60$ for $c = 95 \times 10^{-3}$. It appeared to us that the problem could be attacked in another way. If we have good determinations of k_c and k_d at corresponding concentrations, it is evident that we can calculate α by eliminating k_3 from equations (1) and (2), namely,—

$$\alpha = \frac{k_2}{k_w} \frac{k_d}{k_c}.$$

Here k_2 is well established. Most workers have taken too high a value for k_w. For 25°, McCoy used $k_w = 1\cdot2 \times 10^{-14}$, Auerbach and Pick $k_w = 1\cdot05 \times 10^{-14}$. The later determinations of Kanolt (*Carnegie Inst. Publication*, No. 63) give decidedly lower figures, namely, $0\cdot82 \times 10^{-14}$ at 25°.

Auerbach and Pick have recalculated Shields' values for k_d as follows:—

c (equivalents).	k_d.
$380\cdot0 \times 10^{-3}$	$8\cdot16 \times 10^{-5}$
188·0	9·50
95·4	11·30
47·6	12·60

The figures, plotted on logarithmic paper, lie [illegible] nearly on a straight line. McCoy gives values for [illegible] which are subject to correction for the diminished solubility of carbonic acid in saline solutions, as shown by Stieglitz (*loc. cit.*):—

c.	k_c uncorrected.	k_c corrected
100×10^{-3}	5290	5397
300	4460	4691
1000	3120	3726

When k_c is plotted against log c (where c = concentration in mgrm.-equivalents per litre), the results lie nearly on a straight line:—$k_c = 8739 - 1671 \log c$. We thus get values for k_c corresponding with the concentrations in Shields' experiments.

c.	k_d.	k_c.	α calculated.
$95\cdot4 \times 10^{-3}$	$11\cdot30 \times 10^{-5}$	5400	0·775
188·0	9·50	4970	0·708
380·0	8·16	4450	0·680

The values for sodium acetate, according to Kohlrausch, are:—

c.	α.
$95\cdot4 \times 10^{-3}$	0·785
188·0	0·739
380·0	0·660

The results are close enough to show that no great error will be made by taking the dissociation of the sodium bicarbonate as equal to that of the acetate. The dissociation of sodium chloride is decidedly greater.

The empirical formula for $k_c = 8739 - 1671 \log c$ serves to express the results between $c = 1000$ and 100, but does not allow us to calculate the value at infinite dilution. If, however, by experiments at the highest possible dilutions we can obtain an approximation to $\frac{k_2}{k_3} = k_c \frac{\alpha^2}{\beta}$ at such dilutions that $\alpha^2 = \beta$, we should have data for calculating β, at least approximately, since—

$$\beta = \frac{k_c}{k_2/k_3} \alpha^2.$$

In the experiments to be described, we determined k_c at dilutions $c = 12\cdot5 \times 10^{-3}$, $c = 10 \times 10^{-3}$, and even $c = 5 \times 10^{-3}$, and found that it approached a maximum value of 7124, which we take as $\frac{k_2}{k_3}$.

This gives us the value of $k_3 = 4\cdot27 \times 10^{-11}$ and—

$$k_d = \frac{k_w}{k_3} = 19\cdot2 \times 10^{-5}.$$

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* *Transactions of the Chemical Society*, cxi., 1917.

It also enables us to calculate β from the formula—

$$\beta = \frac{k_c}{7124}\,\alpha^2.$$

Thus we get:—

c.	k_c.	α.	α^2.	β.	$1{\cdot}104 - 0{\cdot}323 \log c$.
100×10^{-3}	5397	0·783	0·613	0·464	0·464
300	4691	0·700	0·490	0·323	0·311
1000	3726	0·525	0·275	0·144	0·144

It will be found that if β is plotted against $\log c$ the result is a straight line, $\beta = 1{\cdot}104 - 0{\cdot}320 \log c$.

This formula will enable us to evaluate β approximately between $c = 100 \times 10^{-3}$ and $c = 1000 \times 10^{-3}$. It probably holds good even at far smaller concentrations, since the formula $8739 - 1671 \log c$ gives for $c = 10 \times 10^{-3}$ a value 7068, against 7124 found.

Since $\alpha^2 = 7124 \frac{\beta}{k_c}$ it follows that α is very well represented by the formula—

$$\alpha^2 = 7124\,\frac{(1{\cdot}104 - 0{\cdot}32 \log c)}{8739 - 1671 \log c}.$$

The following values for α and β are calculated for round concentrations.

The concentrations are mgrm.-equivalents per litre:—

$c \times 10^3$	β.	α.	$\frac{\alpha^2}{1-\alpha}\,c$.
50	0·560	0·822	$190{\cdot}4 \times 10^{-3}$
100	0·464	0·782	281·6
200	0·368	0·731	398·6
300	0·311	0·694	472·4
400	0·271	0·663	523·0
500	0·240	0·636	556·8
700	0·194	0·588	588 9
800	0·175	0·566	592·4
1000	0·144	0·525	579·4

NOTE.—These figures are carried out to three decimal places for purposes of calculation, but it is not of course supposed that they are significant to anything like this degree.

These values represent the activity of sodium carbonate; that is to say, the active mass (as regards the CO_3 ion), and of sodium bicarbonate (as regards the HCO_3 ion) in equilibrium with each other and with carbonic acid. Those for α are founded on the ionisation of sodium acetate, calculated from the conductivity. The values for β are much smaller than would be expected from analogy to sodium sulphate, even after allowing for the presence of an intermediate ion, $NaSO_4$ (Harkins and Bray, *loc. cit.*).

There is, however, evidence, shortly to be presented, that β really corresponds with the concentration of the CO_3 ion, and that the dissociation is not represented by $Na_2CO_3 = 2Na + CO_3$, but by $Na_2CO_3 = Na + NaCO_3$ and $NaCO_3 = Na + CO_3$.

In the former case, the sodium ion concentration would be $2[CO_3] = 2\beta c$, where c is the molecular (not equivalent) concentration, whilst the non-ionised sodium carbonate would be $(1 - \beta)c$. In the latter case the sodium ion concentration will be greater, $[Na'] = 2[CO_3] + [NaCO_3]$, whilst the non-ionised carbonate will be smaller, $C_{Na_2CO_3} = c - [CO_3] - [NaCO_3]$.

If α be the degree of ionisation of sodium carbonate in the first stage, we shall have $C_{Na_2CO_3} = c(1 - \alpha)\,[CO_3] = c\beta$; also, since $c = [CO_3] + [NaCO_3] + C_{Na_2CO_3}$, we have—

$$[NaCO_3] = c - [CO_3] - C_{Na_2CO_3} = \\ = c - c\beta - c(1 - \alpha) = c(\alpha - \beta).$$

Further, $[Na'] = 2\beta c + c(\alpha + \beta) = c(\alpha + \beta)$.

In the mixtures such as we have been dealing with, in which the bicarbonate largely preponderates, we have assumed α to be the same as that of sodium acetate at the same total sodium concentration. In this case, the assumption will not be far from the truth.

In seeking to apply the results to solutions of pure carbonate, some other assumption with regard to the first-stage ionisation will have to be made, since the sodium ion concentration of a solution of pure carbonate is undoubtedly less than that of a solution of bicarbonate of the same equivalent concentration.

It may be said that, for the same reason, the value of β will be different in a decinormal solution of pure carbonate from what it would be in a mixture consisting chiefly of bicarbonate. However, in McCoy's experiments the carbonate varies from a trace to 32 per cent, whilst in those of Shields it varies from 100 per cent to 50 and 20 per cent without showing any noticeable drift in the constant. As a first assumption, we shall assume that β is the same in all mixtures of carbonate and bicarbonate of the same total sodium concentration.

Experiments on the value of $k_d = \frac{k_w\,\beta}{k_3\ \alpha}$ for pure carbonates would enable us to test the question.

As regards α, several assumptions may be made.

1. That $\frac{[Na] + [NaCO_3]}{[Na_2CO_3]} = k_a$ is the same as for solutions of sodium acetate at the same sodium ion concentration (Harkins and Bray, *loc. cit.*)

2. That the degree of ionisation, according to the first stage, $Na_2CO_3 = Na + NaCO_3$, is the same as that of sodium acetate at the same total sodium concentration.

3. That it is the same as that of sodium acetate at the same molecular concentration.

4. That it is the same as that of sodium acetate at the same sodium ion concentration.

Of these, (1) and (4) require us to know approximately the total sodium ion concentration. This could be obtained on assumption 2 or 3, and then corrected by a series of approximations.

Assumption 1 we think is very doubtful, since k_a varies with concentration, and we do not know that its variation is dependent on the sodium ion concentration when $[NaCO_3]$ and $[Na]$ are not present in equal quantity.

In the present dissociation $\mathrm{Na\bar{A}} = \mathrm{Na} + \bar{\mathrm{A}}$, the negative and positive ions are equal in number, but in dissociation $Na_2CO_3 = Na + NaCO_3$ they are not, since $[NaCO_3]$ is reduced and $[Na]$ increased by the further reaction $NaCO_3 = Na + NaCO_3$.

Assumption 3 has been used in the case of sodium bisulphate with success by Noyes (*Carnegie Inst. Publication*, No. 63). We may use it as an approximation, and calculate the value under assumption 4 therefrom (c = mgrm.-molecules per litre).

Under assumption 3 we have the following results:—

$2c$.	c.	α.	$(1-\alpha)$.	β.	$(\alpha-\beta)$.	$(\alpha+\beta)$.
100	50	0·822	0·178	0·464	0·358	1·286
400	200	0·731	0·269	0·271	0·460	1·002
1000	500	0 636	0·364	0·144	0·492	0·780

$2c$.	c.	$[Na_2CO_3]$.	$[NaCO_3]$.	$[CO_3]$.	$[Na]$.	$k_a \times 10^3$.	$k_b \times 10^3$.
100	50	8·88	17·9	23·2	64·3	129·7	83·2
400	200	53·70	92·0	54·3	200·6	343·6	118·3
1000	500	181·80	246·1	72·0	390·1	528·1	114·1

If we use these figures for the sodium concentration to obtain the degree of dissociation, α' on assumption 4, and recalculate the sodium concentration therefrom, we shall obtain the following values:—

$2c$.	c.	α'.	$(1-\alpha')$.	β.	$(\alpha-\beta)$.	$(\alpha'+\beta)$.
100	50	0·80	0·20	0·464	0·336	1·264
400	200	0·69	0·31	0·271	0·419	0·961
1000	500	0·58	0·42	0·144	0·436	0·724

$2c$.	c.	$[Na_2CO_3]$.	$[NaCO_3]$.	$[CO_3]$.	$[Na]$.	$k_a \times 10^3$.	$k_b \times 10^4$.
100	50	10·0	16·8	23·2	63·2	106·0	87·0
400	200	62·0	83·8	54·3	192·2	259·0	124·0
1000	500	210·0	218·0	72·0	362·0	376·0	119·0

k_a is the value of the factor—

$$\frac{[\mathrm{Na}] \times [\mathrm{NaCO_3}]}{[\mathrm{Na_2CO_3}]}$$

and—

$$k_b = \frac{[\mathrm{Na}] \times [\mathrm{CO_3}]}{[\mathrm{NaCO_3}]}.$$

It is to be observed that k_b (which is concerned only with ions) is not greatly affected by the assumption as regards α, and is more nearly constant than k_a, which involves the concentration of the non-ionised salt.

The value of k_a increases with the concentration, but on either assumption is less than that for sodium bicarbonate (or acetate) at the same molecular concentration or sodium ion concentration.

To be continued).

THE OCCURRENCE OF GERMANIUM IN MISSOURI AND WISCONSIN BLENDES.*

By G. H. BUCHANAN.

Of the fifty or more elements which we usually distinguish as rare, few are more worthy of the distinction than the element germanium. Discovered in 1886 by Winkler in a new silver mineral, argyrodite, and identified by him as the eka-silicon of Mendeléeff, it has dropped back into oblivion since the days of this classic work, until to-day it is one of our least known elements. With but few exceptions our entire knowledge of the properties of the element is due to Winkler. According to Urbain (*Comptes Rendus*, cl., 1758) the material worked over by Winkler for the preparation of germanium was a mixture of argyrodite with other minerals, and did not contain more than 0·36 per cent of argyrodite. Since the germanium content of argyrodite is 6 to 7 per cent, the germanium content of his raw material could only have been between 0·02 and 0·03 per cent. From this material Winkler obtained 80 kilos. of mixed metallic sulphides which yielded 156 grms. pure germanium.

Argyrodite, the richest source of the element heretofore known, has proved exceedingly rare, and during the thirty years that have elapsed since the work of Winkler only a very few additional sources of the element have been brought to light.

Krüss has reported the presence of 0·1 per cent germanium in euxenite. Its occurrence in samarskite, tantalite, and niobite has been reported and denied a disagreement which is not surprising in view of the complexity of these minerals. Two other sources have been more recently discussed. Urbain (*Comptes Rendus*, cxlix., 602) by spectroscopic methods detected germanium in thirty-eight out of sixty-four blendes from various localities. Taking 550 kilos. of one of these, a Mexican blende, he obtained from it 5 grms. pure germanium. Bardet (*Comptes Rendus*, clviii., 1278), also by spectroscopic methods, detected traces of germanium in certain French mineral waters. Since the recovery of germanium from blendes by the method of Urbain was long and costly, he believed that the residues from these mineral waters might yield sufficient germanium to provide for the needs of scientific study. From 100 kilos. of residues, representing 250,000 litres of mineral water, he obtained 60 mgrms. $\mathrm{GeO_2}$.

A more recent report of the occurrence of germanium is due to W. F. Hillebrand and J. A. Scherrer (*Journ. Ind. Eng. Chem.*, 1916, viii., 225), in a paper on "The Recovery of Gallium from Spelter in the United States," mention is made of an examination for germanium of a number of blendes, carried on at the Bureau of Standards by Dr. K. Burns. By the use of the spectroscope germanium was identified in several of these, notably in a Missouri sulphide. A short paper by the writer was published in the *Journal of Industrial and Engineering Chemistry* in July, 1916, p. 585, relating to the identification of germanium in zinc-bearing materials. At that time it was not possible to give details as to the origin of the rich germanium-bearing material. It is the purpose of the present paper to discuss the nature of this material, which now appears to be the richest source of the element known.

During the summer of 1915 there was brought to the writer's attention an oxide of zinc which had been prepared from spelter residues by the American process. A chemical examination revealed the presence of considerable quantities of an unusual constituent, which was identified as the element germanium.

The identification tests consisted in a distillation of the oxide of zinc with hydrochloric acid, a slow current of chlorine being bubbled through the solution during boiling to prevent distillation of arsenic. The strongly acid distillate was diluted and saturated with hydrogen sulphide. A voluminous white precipitate was formed which was readily soluble in alkalis and which dissolved in water, although more slowly. The sulphide was slowly reprecipitated from its aqueous solution upon addition of strong acids. The addition of hydrofluoric acid to the aqueous solution of the sulphide, followed by saturating the mixture with solid potassium chloride, produced a greyish gelatinous precipitate, the double fluoride of potassium, and germanium.

A roughly quantitative determination of the ratio $\mathrm{GeO_2} : \mathrm{GeS_2}$ gave the value 0·747. The theoretical ratio, assuming 72·5 for the atomic weight of germanium, is 0·766. The sulphide precipitate was weighed without washing free from precipitated sulphur, since the usual alcohol-carbon bisulphide washing caused the precipitate to run through the asbestos Gooch. The presence of sulphur in the precipitate when weighed would, of course, lower the ratio. Bearing this in mind, the agreement between calculated and observed values is fairly close.

By distilling weighed samples of the oxide of zinc with chlorine and hydrochloric acid, and precipitating and weighing the sulphide, the value $\mathrm{GeO_2} = 0{\cdot}25$ per cent was obtained.

A sample of the oxide of the element, prepared by ignition of the sulphide and treatment of the residue with nitric acid, was examined at the Bureau of Standards with the spectroscope and was reported, "Germanium, principal constituent."

As has been stated, the oxide of zinc in which this considerable amount of germanium was detected was prepared from spelter residues. The attempt was now made to locate geographically the source of the element.

The residues in question were mixed residues from Joplin and Wisconsin ores. An examination of a number of oxides of zinc prepared from ores from various localities, including those made from Missouri and Wisconsin ores, was now undertaken. For this work a delicate test for the presence of germanium was required. The following procedure was applied with success to a large number of samples; the details are those which were found necessary with this class of material. The essential details of the method are due to A. A. Noyes.

Weigh a 100 grm. sample of the oxide of zinc into a litre distilling flask connected with a water-cooled condenser, and add 200 cc. concentrated hydrochloric acid. Pass chlorine into the mixture until the gas appears in the receiver of the condenser, and then heat the mixture to boiling and distil to about half volume, continuing the passage of a slow current of chlorine. Dilute the distillate with an equal volume of water, and pass hydrogen sulphide into it for at least thirty minutes. If no precipitate is formed (other than the usual opalescence due to sulphur) germanium is absent. If a precipitate is formed filter it off on a small paper and wash it with a very little cold water.

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* Presented at the Symposium on the Chemistry and Metallurgy of Zinc, American Chemical Society, April 10, 1917. From the *Journal of Industrial and Engineering Chemistry*, ix., No. 7.

Place the paper containing the precipitate in a flask with about 150 cc. water, boil for fifteen minutes, and filter. To the filtrate add 50 cc. concentrated hydrochloric acid, cool, and treat with hydrogen sulphide as before. A white flocculent precipitate indicates the possible presence of germanium.

Filter on a small paper, and wash once with a little cold water. Pour ammonia through the filter, receiving the solution and washings in a platinum dish. Evaporate to dryness. Moisten the residue with concentrated nitric acid, and evaporate to dryness again. When dry, ignite for a few minutes.

To the residue add a very little water and a few drops of hydrofluoric acid, saturate with solid potassium chloride, and allow to stand in the cold for fifteen minutes. If germanium is present a greyish gelatinous precipitate is formed, soluble on heating, or diluting the solution.

The presence of germanium is not reported unless this last confirmation test is obtained.

With this procedure positive results were obtained with both Joplin and Wisconsin separator ores. Positive results were also obtained from Mineral Point "special leaded oxide of zinc," from an oxide made from a Mexican ore (La Bufa), and from one or two others. Negative results were had from two other Mexican ores, from ore from Austinville, Va., from Mineral Point "prime oxide of zinc," and from New Jersey ores ("XX. oxides"). In all cases where positive results were obtained the amounts detected were very much less than were met with in the oxide made from spelter residues, probably not one-tenth as much. It is probable that the procedure described would detect as little as 0·01 per cent germanium in an oxide of zinc.

It is evident from these results that the germanium content of the residuum may have been derived from either the Wisconsin or the Missouri ore, or from both of them, and that it has been greatly concentrated during the metallurgical treatments which it has undergone. The treatment in the spelter retorts and in the oxide fires has carried on this concentration on an enormous scale, and we have, as a result, an abundance of a material much richer in germanium than the original ores.

The properties of the substance as given in the literature explain the nature of this concentration. The metal is said to be readily obtained by reduction of the oxide with carbon at a red heat, so that under the conditions prevailing in the spelter retort the germanium must be present in the elementary state. It is not markedly volatile at 1350° C. Accordingly, while the zinc was distilling off into the condenser the germanium *for the most part* remained behind, and was discharged with the residues. The qualification seems necessary, since Uhler has detected traces of germanium in the leady residues from the redistillation of low grade metal (Browning, "Introduction to the Rarer Elements," 4th edition, p. 84). In the zinc oxide furnaces the germanium burned to oxide and passed off with the zinc smoke into the bags.

It is possible to obtain a rough approximation of the amount of germanium in the original ore by assuming a zinc oxide content of 10 per cent for the residues and of 50 per cent for the original ore. Assuming in all cases complete recoveries, the GeO_2 content of the residues would have been one-tenth that of the oxide of zinc, or 0·025 per cent, and that of the original ore would have been approximately 0·01 per cent.

The work reported in the preceding paragraphs was carried on by the writer in the Research Laboratory of the New Jersey Zinc Company at Palmerton, Pennsylvania, to the officials of which company the writer is under obligations for permission to publish these results. Through the kind offices of Mr. George C. Stone, of the New Jersey Zinc Company, a supply of the germaniferous oxide of zinc has been furnished the Massachusetts Institute of Technology for study. This work has already been begun.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

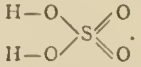
By IRVING LANGMUIR.

(Continued from p. 43).

Theories of Chemical Constitution.—The fact that each atom in a crystal is usually combined with a larger number of adjacent atoms than corresponds to its valence is not in conflict with recent theories of the constitution of chemical substances.

A. Werner ("Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie," Braunschweig, 1905) has made a very extensive study of complex inorganic compounds, and as a result has established a theory of residual or secondary valence.

In accordance with the ordinary theory of valency which has proved so invaluable in organic chemistry, it has been customary to assign structural formulæ of similar type to inorganic compounds. Thus the graphic formula for sulphuric acid is often written—



Whereas among organic compounds the structural formulæ can be determined with certainty, and undoubtedly correspond to the actual arrangement of the atoms in the molecules, no such certainty is ever found in the case of complex inorganic compounds. As a result, such formulæ have served no useful purpose in the development of inorganic chemistry. In fact, Werner claims that the common acceptance of such conceptions was responsible for the fact that our knowledge of the constitution of inorganic compounds failed to progress for so many years.

Werner (*loc. cit.*, p. 42) then shows clearly that such formulæ are untenable. In the first place, the formula would lead to a sharp distinction between the combination of oxides and halides, whereas such a distinction does not actually exist. A proper theory should show a close relationship between such reactions as—

$$K_2O + SO_3 = K_2SO_4$$

and—

$$KCl + AuCl_3 = KAuCl_4.$$

The same kind of relations exist with complex cyanides, nitrates, &c,, and these cannot be accounted for by the ordinary theory of valency.

Secondly, the ordinary theory would indicate that oxides such as OsO_4, RuO_4, &c., should easily form acids by combination with water. Actually, it is found that the number of molecules of water which can be taken up by an oxide does not bear any definite relation to the number of doubly bound oxygen atoms.

Several other good reasons are given against the ordinary graphic formula for such compounds.

Werner then proceeds to show that the ordinary conception of (primary) valence applies (except in organic compounds) practically only to compounds of the first order; that is, to simple compounds containing not more than two elements, such as H_2O, NaCl, SO_3, &c.

Compounds of higher order are formed when compounds of the first order combine together. Thus, Werner draws no sharp distinction between the combination of P_2O_5 and Na_2O to form Na_3PO_4, and such a process as the taking up of "water crystallisation" by a salt such as $BaCl_2$ to form $BaCl_2.2H_2O$

When two elements combine to form a compound of the first order, their primary valences become saturated. But there is still a field of force around the molecule which enables it to combine with other molecules to form compounds having almost any degree of stability. The molecules are then said to be held together by residual or secondary valence.

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* From the *Journal of the American Chemical Society*, xxxviii No 11.

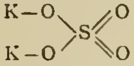
Werner gives the following definitions of primary and residual valency:—

(*a*) "Primary valence serves to unite those simple or complex radicals which can exist as separate ions or whose chemical combining power is equivalent to an ionisable radical."

(*b*) "Residual valence represents the affinity that binds together radicals which can neither act like nor be equivalent to separate univalent ions."

As illustrations of primary valence, he gives $-Cl$, $-Na$, $-NO_2$, $-CH_3$, and for residual valence, $:OH_2$, $:NH_3$, $:ClK$, and $:CrCl_3$.

R. Abegg (*Zeit. Anorg. Chem.*, 1904, xxxix, 330; 1906, l., 309; and *Zeit. Physik. Chem.*, 1909, lxix., 1) advanced a somewhat similar theory of the constitution of inorganic compounds. He looks upon salts of oxygen acids, for example, as consisting of basic and acid oxides held together by secondary valence. He considers Berzelius's idea of the structure of such compounds ($K_2O.SO_3$, for instance) to be much preferable to the structural or graphic formula—



and gives many good reasons to support his contention.

Stark has developed a theory of the mechanism of chemical valency based on the electron theory. (*Jahr. d. Radioakt. und Elek*, 1908, v. 125; *Prinzipien der Atom Dynamik*, iii.; "Die Elektricität im Chemischen Atom," Leipzig, 1915; a short description of Stark's theory of valence was given by Misses Hahn and Holmes in *Journ. Am. Chem. Soc.*, 1915, xxxvii., 2611; this article is essentially an abstract of Paul Ruggli's book, "Die Valenzhypothese von J. Stark vom Chemischen Standpunkt," Stuttgart, 1912). This electroatomic theory gives symbolically a very satisfactory picture of the different types of valence. According to Stark, portions of the surfaces of atoms contain an excess of positive electricity. In the neutrel atom one or more electrons are held close to the surface of the atom by this positive charge. Compounds are formed when the lines of force from one of these "valence electrons" reach out and end on the positive areas of other atoms. In the case of strongly polar compounds, an electron is almost wholly drawn over to the atom which it holds in combination. Primary valences are due to a pair of valence electrons whose field binds two atoms together. The stray electric field in the space around the resultant molecule is the cause of the residual valence. This theory accounts particularly well for the gradations between primary and secondary valence.

Thus, when two atoms combine chemically, they are held together by certain electrons which are common to both atoms. Bohr's model of the hydrogen molecule assumes a similar function of the electrons. According to Bohr's theory, a hydrogen atom consists of a positive nucleus around which (at a distance of $0{\cdot}55 \times 10^{-8}$ cm.) an electron revolves with very high speed. The hydrogen molecule, on the other hand, consists of two hydrogen nuclei (at a distance apart of $0{\cdot}60 \times 10^{-8}$ cm.) and two electrons which revolve in an orbit in a plane perpendicular to the line joining the nuclei. The radius of the orbit of the electrons is $0{\cdot}52 \times 10^{-8}$ cm. In the hydrogen atom the electron forms part of the atom. When two atoms combine the two nuclei share the two electrons equally. If the two atoms separate again, there is an even chance that they will have exchanged electrons. The two electrons held in common by the two nuclei hold the molecule together and are thus equivalent to the bond by which we ordinarily imagine two univalent atoms to be jointed. This model of the univalent bond is remarkably similar to that proposed by Stark.

J. J. Thomson (*Phil. Mag.*, 1914, xxvii., 757) has also developed a theory of the mechanism of chemical affinity. On the whole, his theory is very much like that of Stark. Thomson considers that the electrons near the surface of an atom, together with the positive charge in the core of the atom, constitute one or more electric doublets which exert forces not only on free electrons or ions in their neighbourhood, but also on other electric doublets. The force of attraction between such doublets varies much more rapidly with the distance than the inverse square. Thomson uses the dielectric constant of the substance in the gaseous condition as a measure of the moment of the electric doublets. In this way he concludes that there has been an actual transfer of an electron from one atom to another in such compounds as H_2O, NH_3, SO_2, HCl, CH_3OH, C_2H_5OH, and CH_3Cl, even when these are in the gaseous condition. This "intramolecular ionisation" greatly increases the moment of the doublet by increasing the distance between the charges. In other types of compounds, however, Thomson believes that the atoms are electrically neutral and are held together by one or more doublets on each atom. As compounds of this type he cites H_2, O_2, N_2, Cl_2, CO, CO_2, CS_2, CCl_4, C_6H_6, CH_4, N_2O.

It should be noted that Stark's theory recognises both these types and indicates how there may be all possible gradations between these extremes.

Thomson also believes that the more complex compounds are "molecular compounds" in which simple molecules are held together by the stray field around the molecules. In the first paragraph of his paper he says: "These forces will be exerted by the atom not merely on the atoms which are associated with it in the molecule of a chemical compound, but also on the atoms in other molecules, giving rise to forces between the molecules, and producing thereby the intrinsic pressure and surface tension of liquids, latent heat of evaporation, cohesion of solids and liquids, the rigidity of solids, and so on. These physical phenomena are the effects of forces between different molecules, whereas chemical affinity and chemical phenomena in general are the effects of forces having the same origin, but acting between the atoms of the same molecule."

We shall see that this division of solids and liquids into molecules is very arbitrary and that the same kind of chemical relationships exist between these forces, which Thomson calls physical, as exist among the forces which cause the formation of molecular compounds.

In regard to saturated valence, Thomson considers that two electrons are involved in holding two univalent uncharged atoms together. In this respect his theory is like those of Stark and Bohr. He points out, however (as Stark has also done), that by this theory three univalent atoms may be held together in the form of a ring, one electron being located between each pair of adjacent atoms. He says: "The difference between the theory we are considering and the accepted theory of valency may be expressed by saying that not only is every possible valency compound on the old theory a valency compound on this theory, but every compound which would be a valency one on the old theory if the valency of every element was doubled, would be a valency compound on the new, with the atoms retaining their original valency. This only applies to the compounds when the atoms are uncharged; when the atoms are charged the valency conditions are the same as on the old theory."

This theory would seem to fit in badly with the facts of organic chemistry, for we find no evidence of organic compounds in which carbon acts as if it had a valency of eight or hydrogen a valency of two. But in the formation of crystals this theory suggests an explanation of the divided valence observed in crystals of the spinel group. For instance, it was found in magnetite that the *di*valent iron atoms were surrounded by *four* symetrically placed oxygen atoms, while the *tri*valent iron atoms were surrounded by *six* oxygens.

An extremely important theory of the "Atom and Molecule" is that recently described by G. N. Lewis (*Journ.*

Am. Chem. Soc., 1916, xxxviii., 762). Substances are classified into two general groups: polar and non-polar. The polar type, represented by H_2O, NH_3, NaCl, &c., is characterised by reactivity, high dielectric constant, tendency to form molecular complexes, &c. Tautomerism is a "predominant trait of most inorganic substances (polar type), which behave as if a great variety of forms were existing together in extremely mobile equilibrium."

For this reason Lewis (*Journ. Am. Chem. Soc.*, 1913, xxxv., 1418) believes that the constitution of the more complex inorganic compounds cannot be represented by any single structural formula.

We shall see that these ideas on tautomerism will prove of value in connection with a study of the constitution of liquids.

(To be continued).

SHALL GREAT BRITAIN AND AMERICA ADOPT THE METRIC SYSTEM?*

Mr. H. L. Sulman said he had the honour to open a debate of exceptional importance, but regretted that he could not approach the subject with impartiality, or start the discussion upon an even keel, as his opinions were already strongly polarised; he was in complete sympathy with the author in protesting against the attempt to foist the Metric System of weights and measures upon the mining, metallurgical, and other industries of English-speaking people.

He had been chairman of the "Weights and Measures Committee" of the Institution of Mining and Metallurgy, which for several months during 1906-07 was engaged in standardising the mining and metallurgical measures employed throughout the British Dominions; as one result of its work that committee found itself unable to recommend the adoption of the Metric System, this question having been specifically referred to the committee for consideration.

It had been circulated to all members so far as they could be reached by post, in the terms: "Do you consider that the general adoption of the Metric System of weights and measures would be feasible in mining and metallurgical work, or would this in your opinion lead to undue dislocation?"; 283 answers were received which were almost evenly balanced—viz., for the adoption, 133; against adoption, 130; undetermined, 20. No recommendation could therefore be made.

He might say he entered upon the investigation strongly favouring the Metric System, and believed this to have been the case also with most of his colleagues; they also had the advantage, on two or three occasions, of the light and leading of the secretary of the Decimal Association, an official advocate of the Metric System; therefore they commenced not only with a predilection towards it, but had expert advice to shape their opinions. Nevertheless, the result was that they became convinced that the introduction of the Metric System would cause chaos for years, and would thus be disastrous to the industry it was their duty to aid. Had the 133 members who voted in favour of adoption been able to have the same data before them, he thought their number would have been materially reduced.

They were mainly concerned with the industries of mining and metallurgy, and it would be difficult to choose an authority more competent to deal with the incidence of the Metric System on these than Mr. Ingalls, whose work in the collation of statistics of the metalliferous mines and markets of the world was unique; if anyone had had the opportunity of appreciating the strong points of the Metric System, surely it was the author. That he had so completely decided against its compulsory adoption was as strong an argument of experience as he (the speaker) could desire.

He would leave the practical engineers present to indicate what was likely to be the dislocation involved in time, effort, and money, and the scrapping of perhaps millions of pounds' worth of plant, and what were the advantages to be gained, by changing over from the units now used throughout the British Empire to those of the Latin and of the Central Powers of the Continent. It was curious to recall that here, on "Empire Day," they were engaged in discussing a proposal to abandon standards of British origin and of world-wide employment, to reject modifications which would bring us more closely into line with our self-governing Dominions and with the United States of America, and to substitute therefor a mathematical Utopia, of limited industrial scope, and to take a decision which would rejoice our enemies in regard to their after-war trade. Surely this, as the author said, was the "tail wagging the dog" with a vengeance!

If he spoke in generalities which might appear threadbare, he at least performed a service in thus clearing the ground for later speakers; further, the value of generalities was sometimes over discounted. No one was so stupid as to quarrel with a proposal for the decimalisation of units within due limits; what they opposed was change of the units to be decimalised. They were asked to give up the basic units of foot and lb. for the mètre and kilogramme, but the latter were only pseudo-scientic substitutes; the mètre itself was based upon an erroneously measured fraction of an earth-quadrant, and had no more absolute scientific value than any other empirical unit. It certainly had not the sanction of such centuries of usage as had the former, nor to the extent to which they had become part of our senses and automatic perceptions in visualising weights and measures.

The advocates of the Metric System adopted the attitude that English-speaking countries used non-decimal weights and measures which were chaotic in number and subdivision; that these required years to learn, and were at best but a tangle of obsolete absurdities. They instanced the dual use of Troy and Avoirdupois weight for the same ore; and paraded the scruple and drachm, the pint and the pottle, the bushel, hogshead, and acre, for derision, alleging them to have little or no correlation, and therefore to waste a vast aggregate of human energy in the simple conversions of weights into volumes, and so on. Their view was that if we wished to decimalise, simplify, and render uniform our system of weights and measures, the only plan was to throw the whole lot overboard, lock, stock, and barrel, our only true salvation being the Metric System; that we were bound to adopt the gramme and the mètre because the ton, the lb., the mile, the foot, and the gallon were hopeless to decimalise. These arguments were as unanswerable as that the cure for corns is amputation of the leg.

The agitation to abandon our present standards and supersede them by the Metric System appeared to lack perspective. It was the hobby of the pure scientist who, from experience of its unquestioned convenience in the laboratory, and its general adoption for expressing physical constants, betrayed impatience that national and industrial conditions should lag behind his laboratory practice and mathematical ideals. He appeared unable, or unwilling, to realise the vast dislocation of effort and material entailed by what he regarded as a comparatively simple and easy change. Indicate to him the millions of expenditure and the "time lag" this would involve and he would cheerfully reply, "Yes, perhaps two or three days of our present war expenditure"; and "In but a few years, a generation at most, everybody will think metrically." This lack of tolerance seemed characteristic of the system, which tended to turn philosophers into fanatics, who, when engineers pointed out that the facts of their vast industries were against such wholesale simplification, exclaimed, "Then so much the worse for the facts!"

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* Opening of a Discussion on a Paper by Mr. W. R. Ingalls read before the Institution of Mining and Metallurgy, May 17, 1917 (*Bull.*, No. 152).

But the incursions of the pure mathematician into complex manufacturing technics, such as our own, were not always attended by our complete enlightenment. They would recall that he had proposed to quantify the efficiency of the stamp and the tube-mill, the roll, and the Chilian mill by hypothetical units based upon Kick's law, itself a high-and-dry mathematical conception applicable only to a strictly homogeneous substance, whilst the whole of our crushing practice depended upon the precisely contrary requirement, namely, success in separating the constituents of a heterogeneous mass. So also with the grading of the crushed products; here mathematicians had sought to lead them into complex seriations of aperture-width founded on mathematical ideals difficult of realisation, practically meaningless if realised, and involving conditions of accuracy far beyond the limiting facts of the case. Whilst science has been defined as "measurement" it had been more aptly described as "organised commonsense," and insistence on mathematical perfection when this would lead to disorder in other respects was less science than pedagogy.

A fact sometimes in danger of being missed, was that the Metric System had no exclusive freehold right to decimals; it was open to them to realise many of the advantages which the Metric System loudly proclaimed as its own, by decimalising their standards, so far as desirable, without inviting the chaos for a generation, and the untold expenditure, involved by a change of unit.

Several desirable simplifications were quite easy of adoption. Mr. Ingalls in one of the latter paragraphs of his paper said, "I hope to see the day when our legislatures will cease muddling over the size of barrels and let each industry adopt what suits it best, subject only to the requirement that its capacity in cubic feet and decimals thereof shall be marked upon it. We should like to see Great Britain adopt the ton of 2000 lb. and decimalise her coinage on the basis of the pound sterling. Not to ask Great Britain alone to give way, let us adopt her gallon of 10 lb. of water, if gallon we must continue to use, as no doubt we shall have to for a long time yet. Let both Great Britain and the United States abolish the Troy pound."

That was written in 1917. In 1907 the Institution of Mining and Metallurgy circulated the following recommendation to its membership throughout the Empire: "The word 'ton' shall represent a weight of 2000 lb. Avoirdupois"; followed by the note: "It is advisable to abandon the use of the terms 'hundredweights' and 'quarters' and to express fractions of tons in pounds or decimals of a ton." The next recommendation was that "the word 'gallon' shall represent an Imperial gallon of 10 lb. of water."

In a further recommendation which, whilst not advising the abandonment of the Troy ounce, recognised the desirability of a simpler relationship between weight and value, it was stated that: "The gold contents of ores, determined by assay, shall be expressed in money values as well as weights." This was a tentative step towards simplification, the value of the Troy ounce of gold being taken as 85s. sterling, which incidentally meant that the "pennyweight" of gold was the dollar, within a minute fraction.

It was gratifying to see that what the Institution advised in 1907 the author of the paper now ably and eloquently confirmed.

But as to values, chaos in units still persisted between the "Metric" countries themselves, and the franc, mark, lire, and peseta still required translation from one to the other. On the other hand, as had oftentimes been pointed out, English-speaking peoples had a much wider basis for uniformity of currency in the dollar, *i.e.*, the 100 cents or half-pennies; the cent was of the same value throughout the world, whether in England, the United States, Canada, Australia, New Zealand, South Africa, &c. If it appeared safe, therefore, to prophesy that the dollar would never be superseded by the mark or the franc, it was not unreasonable to hold that the pound would in the future continue to be just as widely employed.

The Metric System, apart from the laboratory, was certainly of value as a species of "Esperanto" in weights and measures, offering a convenient method for translating units of mensuration of one country into those of another; but it was to be hoped that for us its compulsory adoption was as far distant as the compulsory substitution of Esperanto or Volapuk for the English language.

Even decimalisation was not a synonym for salvation. The science of mathematics, with its provinces of decimals, duodecimals, &c., even our very system of numeration, were after all merely human creations, and (like all such conceptions) had a strictly evolutionary history; there was nothing of the nature of "Revealed Truth" about them. Our numeration was decimal of course because of man's possession of ten fingers. Had he evolved a six-digit hand we should doubtless have inherited a duodecimal scale of notation, and it would have been as difficult to think in decimals as in septimals; a position which might not have been without its advantages. Yet before he could count up to ten, man began to think in "twos" and "threes." It did not follow, even yet, that our numerical conceptions were more readily grasped if expressed as decimals. The ordinary man visualised the simpler fractions, the quarter, eighth, sixteenth, &c., much more easily than their decimal equivalents. We were not all professors, and for most these proportions were easier than 0·25 or 0·125, 0·0625, to say nothing of the ponderous mess that decimals make of thirds and sixths.

Any rational system of multiples or divisions would employ the duodecimal as well as the decimal; it was obviously advantageous to have a system of measures capable of division by 2, 3, 4, and 6, rather than by 5 or 10 alone, and according to which simple fractions like thirds, and even 32nds and 64ths, would not run into expressions as long as one's arm.

One frequently heard the Metric System extolled for the extreme simplicity of its calculations; apparently in most cases all that was required was to take a unit or two with a few noughts behind it, and divide or multiply it by another unit, with a tail of noughts, then to take away the number of noughts first thought of, and the result was obvious at a glance. But occasionally the difficulty was to decide where that "damned dot" (as Lord Randolph Churchill expressed it) came in, and a small mistake of a hundred or thousand per cent could readily be made by the very simplicity of the operation. Though, of course, not a serious argument, this contained a percentage of truth which some would secretly acknowledge.

Having now occupied their attention for what the late Sir Frederick Bramwell once called "point 333, &c. of an hour" he would leave the question to its closer debate.

(To be continued).

VIRTUES OF THE WILD WHITE CLOVER PLANT.

I had the opportunity the other day (writes our Agricultural Correspondent) of looking over a farm in South-West Durham, the lessons of which ought to be widely known in view of the new agricultural policy which the war is compelling us to face. This year the plough will be busier than at any time probably within the past twenty-five or thirty years, and since it is of the essence of good husbandry to look ahead, there is now no time to lose in deciding how many, and what, fields the farmer intends to plough down, as his contribution to the increased arable area called for. A great many farmers have already given the subject close attention, so as to effect a change without unduly interfering with the normal round of stock carried.

The paramount purpose, of course, is the increased production of food. Hence, everything turns upon the right kind of land being put under cultivation, as to which, however, a vicious circle tends to be created. Poor pastures, which the farmer might very well be disposed to spare, would be of even less service under wheat or corn; and, on the other hand, the farmer hesitates to intrude upon good, or middling, grass land which has taken so many years to mature, and which would take years (so the argument runs) to put back again, if the need should arise. It is upon this particular difficulty that the experience of the Durham farm which I visited throws an interesting light, pointing a way out of bringing old pastures at once under a course of cropping for the next few years, and then, if it should be found necessary, laying them away again with seed mixtures capable of making good permanent grass inside three, four, and five years, as the case may be—a system rendered possible by calling in aid the wild white clover plant, which, as is now well known acts as a natural fixer of nitrogen from the air, and stimulates the root activity of all other grasses in its vicinity. Indeed, the time may come when a fuller realisation of this invaluable medium will lead to a wide extension of arable cultivation on all farms, bringing selected pastures into rotation at intervals of from four to six years, with great enhancement of fertility, where these pastures are now only in middling condition.

Valuable Field Experiments.

In the past three or four years a series of valuable field experiments have been carried out at Bolam, near Heighington, by Mr. T. G. Robinson, acting under the advice and personal guidance of Mr. Frank P. Walker, M.Sc., Adviser in Agriculture at Armstrong College, and now Executive Officer to the Durham War Agricultural Committee. The farm at Bolam is a typical Durham holding looking south over the dale of the Tees. It lies well up, some of the higher portions being 500 ft. above sea level, while the character of the soil is mostly strong clay, and not too well drained. Many aspects of the work, such as the improvement of pastures by basic slag of high quality, are of great value; but for the moment one is chiefly concerned about the future of pastures proposed to be ploughed down, and with the prospect of dove-tailing these in due course into the ordinary scheme of farm rotation, treating seeds, in fact, as part of the farm's permanent grass for a period of three and four years.

Mr. Walker, whose work, it should be noted, is made possible by the foresighted policy of the Durham County Council and of the Agricultural Education Committee of that body, began his experiments here in the autumn of 1914 by getting Mr. Robinson to plough up a 16-acre field that had been under pasture for 21 years. By way of compensation the holder took an arable field of similar size, and laid it away to grass, which is now in its third year. The soil of this field is typical, as I was told, of the whole farm—strong clay, somewhat brashy, and not over dry; its tendency to bake is just now very obvious under the dry spell. When it was laid away to grass (with wheat and barley) in 1914, Mr. Walker planned for it three different schemes of treatment as regards seeds. The top portion received a seed merchant's ordinary mixture for a three years' ley, with the addition of 1 lb. per acre of wild white clover. The two lower portions received a Cockle Park mixture, containing 3 lb. per acre of wild white clover. In the autumn the stubble was grazed bare with sheep, and at Christmas, 1914, the whole field was topped dressed with half a ton per acre of high quality basic slag, since when it has received no manure whatever. The foggs, however, were heavily grazed with sheep, cow, and horse stock. It was mown for hay in 1915 and 1916, the average yield per acre being over two tons, and I should say that a very much larger crop is coming forward for this year's harvest. But the crucial thing to observe now is the thick, superior sole that has been produced where the extra 2 lb. of wild white clover were sown. On the top portion—you can note the line of division at a glance—there is, indeed, a good root, and the plant is spreading, but the other portions provide quite a soft carpet to the tread, and the effect of the clover stimulus is to be seen in the healthy appearance of the under grass, which will come along as good fogg; in fact, no one could desire a more satisfactory basis for a permanent pasture, while the whole field carries a healthy, virile flush of green. Permanent pasture, however, it is not to be. The experiment has amply paid for itself, and Mr. Robinson will reap an added return no doubt from next year's oat crop, to say nothing of the roots to follow. On another part of the farm I was shown a five-acre field, which two years ago also received a Cockle Park mixture (including 1½ lb. of wild white clover to the acre), and returned last year a bumper crop of clover hay, estimated at 3½ tons to the acre, following a top dressing of high quality basic slag, 10 cwt. to the acre. The seeds are now in their second year, therefore, and look extremely healthy.

Old Pastures Ploughed Up.

Two old pasture fields that have been ploughed out are now under crops. The first that was tackled in 1914 produced in the following year an excellent crop of leader oats, 8 quarters to the acre, having been manured with 2 cwt. of superphosphate and 1½ cwt. of sulphate of ammonia to the acre. Last year, under unfavourable weather conditions, it returned 5 quarters of wheat to the acre, being manured at sowing with 2 cwt. of superphospate and 6 cwt. of high quality basic slag, and top-dressed in the spring with 1½ cwt. of sulphate of ammonia. Now a good half of it is planted with potatoes, well dressed with farmyard manure, and with 3 cwt. of steamed bone-flour and 1½ cwt. of sulphate of ammonia. The rest of the field is being prepared for turnips. Next year the whole will be sown with barley, and seeded away for pasture again, receiving (such is the intention) 3 lb. of wild white clover to the acre. Thus, it will have passed through a thorough course of cropping, and analogous experiments on other parts of the farm give every promise of a permanent pasture of high quality in two and three years—a pasture much superior, in fact, to that which is replaced, and which, by the way, had not been disturbed for more than 20 years.

Another 16 acres of old pasture was ploughed out in 1915, and, with similar manurial treatment, produced a particularly good crop of oats last year; but as it was rather late in ripening, Mr. Robinson was prevented from following on with wheat, as he intended. The field is now under oats again, and, though sown only a month ago, the blade looked particularly well at the time of my visit.

It would be interesting, if considerations of space did not forbid, to allude also to the many other field tests on the virtue of basic slag for improving old pastures; but, after all, the method has by this time so established itself as to be beyond dispute. A further feature of Mr. Walker's work has this novelty—it has demonstrated the practicability of renovating poor pastures without necessarily ploughing them out. The pasture treated here was laid away in 1908, and is now harsh and dry, without a particle of clover showing. In the middle of the field, four small lots were selected for experimental treatment with slag, and slag and potash; in addition, two of the plots were heavily harrowed and re-seeded, with a mixture of wild white clover. This was in 1914, and the result already is astonishing. While the plots that were not re-seeded now show very little advantage for the manurial treatment, the plots which received the seed mixture, in addition, exhibit their superiority almost to the very inch, the value being enhanced quite three-fold, due, of course, to the virile action of the clover plant, which must be regarded as indispensable in laying away permanent pastures. The pity is that the seed should be so expensive. The culture of the plant for seed purposes ought to be established on a larger scale, under native conditions. At present the demand far exceeds the supply, and in consequence farmers with no capital are denied its use, while many others having the capital are loth to pay the high price demanded, even though it may be possible to show that the plant pays for itself whatever the price. Mr. Robinson's farm carries more stock and produces more milk than ever it did. At present he is milking thirty cows, and when I left they were standing in the byres being milked by machines, operated by a small petrol engine. The cleanliness of the byres was particularly noteworthy.—*The Yorkshire Post* of June 7, 1917.

EMPIRE TRADE NOTES.[*]

The Pines of India.

The latest expert reports received by the British Empire Producers' Organisation make it clear that there is a great future before the Indian pine resin industry. Pine resin is commercially exploited in a large number of different ways. It supplies resin for shellac making, soap works, paper mills, oilcloth, linoleum, sealing wax, printing inks, electric insulation, gramophone records, and wheel grease. It also supplies turpentine, the chief solvent in the paint and varnish trades, a mordant in the manufacture of print goods, the basis of synthetic camphor, and an ingedient of boot-polishes, liniments, and embrocations. It has moreover a direct war use, being employed in "setting" shrapnel bullets in shells. At present the United States are responsible for 80 per cent of the world's output of resin and turpentine, France coming second with 15 per cent, and the rest of the world contributing the remaining 5 per cent. To day India is producing annually some 1300 tons of resin and 111,000 gallons of turpentine, a total which does not even meet her own requirements. But only a small fraction of the available pine forests have yet been worked. In the not too distant future India should not only be supplying herself with all the resin and turpentine she requires, but also Java, China, and the Far East.

Beet and Maize Production in South Africa.

The British Empire Producers' Organisation learns from a South African correspondent that an excellent start has been made this year in the export of meat from the Union of South Africa, the figures for the month of March, 1917, being 61,740 cwts., valued at £148,900, as compared with 157,912 cwts., valued at £354,341, for the whole of last year. A large expansion in cattle-rearing in South Africa in the future will to some extent be dependent on the extension of maize-growing, and the Dominions Royal Commission, in its final report recently issued, drew attention to the immense tracts of land in the Transvaal, the Orange Free State, Natal, and the native territories in South Africa which are available for maize cultivation, and stated that, with the increase of settlers on the land, this industry is capable of the widest expansion. The American farmer has shown the best use to which the maize crop can be put; he carries it to final results and realises it in beef. After making ample provision for the needs of the stock on his farm he sells the remaining grain, for which there is always a ready market. In South Africa the feeding of cattle on the maize farm will be a simpler problem than it is in America owing to the mildness of the winter. For the greater part of the year the natural veldt pastures in all the maize-growing districts of South Africa are capable of maintaining stock in good condition. For winter feed, maize cut at the proper stage of growth, then chopped up and cured in a silo, is available.

Empire Cotton.

The belated Government Committee to consider the development of cotton cultivation in the Empire is fortunately a etrong one. It is to be hoped that it will lose no time over its work. Amongst Empire sources of cotton, in addition to those mentioned in the last issue of these notes, both Australia and South Africa are likely to be heard of in the future. In the latter, for instance, excellent cotton is being grown in the Rustenburg district of the Union, and the area of cultivation there has been increased during the last season by between 500 and 600 per cent. During the same season, the British Empire Producers' Organisation understands, 500 lbs. of first-class seed cotton were produced within the Union, while this season's yield is estimated to reach 3 000,000 lbs. Cotton, it should be remembered, has important by-products in cotton-seed cake and cotton-seed oil. The former will, with the development of cotton cultivation, supply a valuable foodstuff for the cattle ranches, to the benefit of the coming great South African meat exporting industry. The latter will replace the present considerable import of this oil into South Africa. It should be noted, too, that though the bulk of Indian cotton is of short staple and unsuitable for the Lancashire mills as at present equipped, a number of improved varieties have been established in recent years, and are already being produced in commercial quantities.

Natural Indigo Outlook.

The production of natural indigo in India has been immensely stimulated during the war by the shortage of the synthetic article formerly produced by Germany in such large quantities. At the war prices ruling, Indian natural indigo has been a most profitable crop, but it has been generally held in this country that when normal prices return it will become unprofitable again in competition with an ample supply of synthetic. The British Empire Producers' Organisation understands, however, that this is by no means so certain as in some quarters believed. Indian indigo has suffered not merely from synthetic competition, but from careless and unscientific methods of production, resulting in an often unsatisfactory and nearly always uncertain article. Strenuous efforts—already attended with some measure of success—are being made in India to remedy the defects of the native product. The dye is being produced in paste form, which is more convenient to the purchaser, and the strength is being brought more nearly to a fixed standard. At the same time, cost of manufacture is being cheapened. The planters are, at all events, making a stroug push to retain the whole, or the bulk, of the trade that the war has brought them, and the outlook in this respect, though still not certain, is at least encouraging.

NOTICES OF BOOKS.

The Origin, Symptoms, Pathology, Treatment, and Prophylaxis of Toxic Jaundice observed in Munition Workers. London, New York, Bombay, Calcutta, Madras: Longmans, Green, and Co. Pp. 106. Price 7s. 6d. net.

This book contains a full report of a detailed discussion, held in January, 1917, by the Sections of Medicine, Pathology, and Epidemiology of the Royal Society of Medicine. Many of the most eminent authorities who bave had special opportunities of studying the subject of toxic jaundice among munition workers were present and took part in the discussion, and very full accounts were given of their experience and opinions. The incidence of the disease was discussed from an administrative point of view by Lord Chetwynd, as managing director of a filling factory for the Ministry of Munitions of War. His opinion that the poison enters the body by the inhalation of toxic fumes is not shared by all investigators, Dr. Benjamin Moore's work, for instance, leading him to the conclusion that the main channel of absorption is the skin and that the inhalation of fumes or dust plays no part. It seems probable that after a certain time workers acquire immunity against the poison, and it also appears that susceptibility varies very much in different people. The symptoms of the disease and its treatment were fully discussed by various speakers, and Fleet Surgeon Munday gave a detailed account of the thoroughly successful methods of prevention.

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[*] Published monthly by the British Empire Producers' Organisation, Kingsway House, Kingsway, London.

The Decimal System of Coinage, Weights, and Measures. By Harry Allcock, M.I.E.E., A.M.I.Mech.E.

This lecture, delivered before the Institution of Civil Engineers in March, 1917, contained a particularly convincing exposition of the arguments in favour of the adoption of the decimal system of weights and measures. The present time is most certainly well suited for the change, and it is highly desirable that the expansion of our overseas trade, which we trust will follow on the declaration of peace, should be unhampered by any such purely artificial circumstance as the use of an unwieldy and peculiar system of weights and measures and coinage. We may safely predict a much increased production of merchandise, and it is essential that every effort should be made to create a correspondingly increased demand for goods of our making. When the coinage systems of the world are studied we find that practically all countries with the exception of the British Empire employ a decimal system, while we also differ from other countries in employing a monetary unit of high value. After reviewing the various proposals which have been made the author expresses the opinion that it would be best to retain the present gold coins and the florin and shilling (of 50 cents), and to adopt a silver quarter of 25 cents, nickel 10 and 5 cent pieces, and 4, 2, and 1 cent bronze coins. It is clear that our adoption of the international metric system of weights and measures cannot be very long delayed, and the author clearly summarises the advantages which must accrue to trade and education when the change is made. Applications for copies of the pamphlet and for permission to reprint may be made to the author at Radbourne, Hale, Cheshire.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 20, May 14, 1917.

The Refractory Properties of Clay.—H. Le Chatelier and F. Bogitch.—Most refractory bricks used for making furnaces are made of clay which consists essentially of kaolinite, $2SiO_2Al_2O_3.2H_2O$, mixed with different impurities, sand, potassic mica, and iron oxide. All foreign bases diminish the refractory qualities; in good clays they should not exceed 4 per cent in amount. Pure clays composed exclusively of kaolinite fuse at 1780°; clays containing much sand fuse at about 1680°, and if they contain more than 4 per cent of iron oxide the melting-point falls to about 1580°. It would naturally be concluded that refractory clay bricks would be used for the construction of industrial furnaces in steel works, but this is not the case, silica bricks being always employed and found satisfactory. It is found that clay bricks gradually soften and lose resistance to pressure, and the authors have investigated experimentally the alteration of shape by pressure at increasing temperatures. Their results agree with those of Mellor and Moore.

No. 21, May 21, 1917.

Bromides of Zirconyl.—Ed. Chauvenet.—With bromine, as with chlorine, zirconium forms three series of compounds. The first includes zirconium bromide, $ZrBr_2$. The second consists of the hydrates of the bromide of zirconyl, $ZrOBr_2$, which does not appear to be capable of existing in the anhydrous state. These hydrates contain 8 and 3·5 molecules of water respectively. The third series comprises the anhydrous complex oxybromide, $ZrOBr_2.ZrO_2$, and its hydrate, $ZrOBr_2 ZrO_2.12H_2O$. At a red heat and in a current of dry hydrobromic acid the complex oxybromide is decomposed into $ZrBr_4$ and ZrO_2.

Anomaly in the Solubility of Sparteine.—Amand Valeur.—When aqueous solutions of sodium carbonate and neutral sulphate of sparteine are mixed according to the temperature and concentration a slight turbidity is produced, or a light oil separates. A turbidity is also produced when aqueous saturated solutions are slightly heated alone, and as dilution is increased a solution is obtained which becomes turbid at temperatures which are higher the greater the dilution. The relation between the concentrations of sparteine and the temperature of the formation of the turbidity has been determined, and it is found that between concentrations of 9 and 18 cc. per 100 cc. the curve showing the results is practically a straight line. A method of determining sparteine can be based on these measurements.

Acidylsemicarbazides and Acidylsemicarbazic Acids.—J. Bougault.—The product obtained by the action of iodine and sodium carbonate on the semicarbazone of phenylglyoxylic acid appears to possess the formula $C_6H_5.CO.NH.NH.CO.NH_2$, while its isomer $C_6H_5.C(OH):N.NH.CO.NH_2$ is prepared by the action of benzoic anhydride on the semicarbazide. Thus compounds belonging to both the theoretically possible series have been prepared. It would be best to call the second acidylsemicarbazid acids and to reserve the name acidylsemicarbazide for the first.

MISCELLANEOUS.

Tungsten Ore.—*The Review of Mining Operations in South Australia* for the half-year ending December, 31, 1915, includes a report by R. L. Jack on a tungsten deposit at Callawonga Creek, hundred of Waitpinga. The field is situated 18 miles by road from Normanville. The rocks of the locality consist of fine-grained quartzite, sandstone, and slate. Schists appear to be present, but were not seen *in situ*. The tungsten ore mineral is ferberite (a variety of wolframite almost free from manganese), occurring in a pegmatite vein associated with quartz, tourmaline, felspar, mica, and patches of kaolin. The ore occurs in irregular pockets. A specimen of clean ferberite gave the following analysis:—Tungstic oxide, WO_3, 71·35 per cent; ferrous oxide, FeO, 26·26 per cent; silica, SiO_2, 0·24 per cent; manganous oxide, MnO, 0·17 per cent; magnesia, MgO, 0·03 per cent; water, H_2O, 1·26 per cent. The lode varies in width from 2 ft. to 6 ft. It has been opened up in the main workings to a depth of 10 ft. over a distance of 120 ft. A second open cut, on a quartz vein carrying pyrite, disclosed two pockets containing 180 lbs. and 3 cwt. of ore respectively.—*Bulletin of the Imperial Institute*, xiv., No. 4.

Separation of Iron from Lead.—J. F. Sacher.—(*Chem. Zeit.*, 1917, xli., 245).—A method for the separation of small quantities of iron from lead depends on the insolubility of basic ferric nitrate. Two grms. of the lead salt are treated with a moderate excess of nitric acid (sp. gr. 1·15), the mixture is evaporated to dryness on a water-bath, and the residue is heated at 100° C. for fifteen to twenty minutes. The residue now contains the iron in the form of a basic nitrate of the approximate composition $2Fe_2O_3.N_2O_5$, or as a hydrate of this compound. Further heating results in a loss of nitric acid, so that the composition of the compound is not constant; but this is not of importance, as the iron still remains in an insoluble form. The residue is then treated with hot water, the insoluble portion is collected on a filter, washed, dissolved in hot dilute hydrochloric acid, and the iron is precipitated as hydroxide from the solution. Should the lead salt under examination contain silicates which are decomposed by nitric acid, the residue obtained after the evaporation of the nitric acid must be heated at 130° C.; lead nitrate is not decomposed at this temperature. If lead sulphate is present the basic iron nitrate must be extracted with hot ammonium acetate solution before it is dissolved in hydrochloric acid. The separation of iron from lead by the above method is so complete that the filtrate from the basic iron nitrate precipitate does not yield any coloration when tested with thiocyanate.—*Analyst*, July, 1917.

THE CHEMICAL NEWS

Vol. CXVI., No. 3011.

STUDIES OF THE CARBONATES.*

Hydrolysis of Sodium Carbonate and Bicarbonate and the Ionisation Constants of Carbonic Acid.

By CLARENCE ARTHUR SEYLER
and
PERCY VIVIAN LLOYD.

(Continued from p. 55).

The Value of $\frac{k_w}{k_3}$.—This we calculated to be $19\cdot2 \times 10^{-5}$ at concentrations of about 10×10^{-3} and under.

In order to check this, we made some determinations of the value by Shields' method, namely, the velocity of hydrolysis of ethyl acetate.

For $c = 100 \times 10^{-3}$ we obtained $k_d = 12\cdot69 \times 10^{-5}$
11·72
12·15
mean, $12\cdot18 \times 10^{-5}$.

This result is rather higher than that calculated from Shields' experiments, namely, $11\cdot6 \times 10^{-5}$.

For $c = 12\cdot5 \times 10^{-3}$ we obtained $k_d = 21\cdot5 \times 10^{-5}$
22·2
21·8

A second series gave:—
$16\cdot8 \times 10^{-5}$
$16\cdot8 \times 10^{-5}$

For some reason, two experiments gave decidedly lower results than the others, but we could see no reason for rejecting them.

The mean of all the experiments is $19\cdot8 \times 10^{-5}$.

The average would give $k_3 = 4\cdot15 \times 10^{-11}$.

The Effect of Sodium Chloride.—For the purposes of another investigation, it was desired to know what effect would be produced on the equilibrium of carbonates and carbonic acid by a salt with a common sodium ion, such as sodium chloride. It was expected that if in a decinormal solution of sodium carbonate the sodium concentration was raised to normal strength by sodium chloride, the value of k_c would be diminished until it had about the same value as in a normal solution of pure carbonate and bicarbonate. It was found that k_c was indeed reduced, but the value was about 23 per cent higher than that in the absence of sodium chloride.

Concentration of carbonate (equivalents).	Concentration o' sodium chloride.	Total Na.	k_c,
$100\cdot0 \times 10^{-3}$	0·0	$100\cdot0 \times 10^{-3}$	5300
100·0	900·0	1000·0	3836
1000·0	0·0	1000·0	3120
12·5	0·0	12·5	7124
12·5	87·5	100·0	6258
100·0	0·0	100·0	5300

Hence, starting with a pure N/10-solution of carbonate, for which $k_c = 5300$, the value of k_c decreases to 3120 when the sodium concentration is increased to N by carbonates of sodium, but only to 3836 when the sodium concentration is due to the chloride. That is to say, the value of k_c will depend, not only on the sodium concentration, but on the ratio of the chloride to the carbonate. Let this ratio be called r, then with $r = 9$ the value of $\frac{k'_c}{k_c} = 1\cdot23$.

For the dilute solutions of carbonate we have for $r = 7$ $\frac{k'_c}{k_c} = 1\cdot18$.

It thus appears that the effect of sodium chloride on k_c is of the same order for dilute or concentrated solutions, and depends upon r, the ratio of chloride to base as carbonates.

The effect of the salt must be due to the alteration of the ionisation of the carbonate and bicarbonate, since, as before,—

$$k'_c = \frac{k_2}{k_3}\,\frac{\beta'}{\alpha'^2} \qquad \frac{k'_c}{k_c} = \frac{\beta'}{\beta}\,\frac{\alpha^2}{\alpha'^2}.$$

It is to be expected that the ionisation of sodium bicarbonate will not be greatly affected by the presence of sodium chloride, but will have much the same value when the total sodium concentration is the same, whatever be the value of r. If this is the case, the effect must be due to the alteration of the ionisation of the carbonate. Putting $\alpha' = \alpha$, we have $\frac{k'_c}{k_c} = \frac{\beta'}{\beta}$.

In order to express the effect of salt, we shall assume that β' has a similar form to β; that is, can be expressed by the formula $\beta' = a' - b' \log c$, where c is the total sodium concentration in mgrm.-molecules. Then—

$$\frac{k'_c}{k_c} = \frac{a' - b' \log c}{a - b \log c}.$$

We have already found $k_c = 8739 - 1671 \log c$.

For k'_c we have at $c = 100$ $k'_c = 5397$. At $c = 1000$ we obtained 3836. This requires correction for the diminished solubility of carbonic acid, which makes it 4581. We then find $k'_c = 7029 - 816 \log c$,—

$$\frac{k'_c}{k_c} = \frac{7029 - 816 \log c}{8739 - 1671 \log c}.$$

When $c = 100$ we have no salt present, and $k'_c = k_c$.

If salt be added, it is evident that $c = 100\,(r+1)$, therefore $\log c = \log (r+1) + 2$, whence—

$$\frac{k'_c}{k_c} = \frac{5397 - 816 \log (r+1)}{5397 - 1671 \log (r+1)} = \frac{1 - 0\cdot1512 \log (r+1)}{1 - 0\cdot3096 \log (r+1)}.$$

Hence generally we have for β (assuming that the effect of salt is the same at other dilutions)—

$$\beta = (1\cdot104 - 0\cdot320 \log c)\,\frac{1 - 0\cdot1512 \log (r+1)}{1 - 0\cdot3096 \log (r+1)}.$$

When no salt is present, $r = 0$; this reduces to—

$$\beta = (1\cdot104 - 0\cdot320 \log c).$$

The effect of the salt was deduced from the experiments on N/10 sodium carbonate, but it must apply approximately to more dilute solutions. For instance, with N/80-solutions, $r = 7$, $r + 1 = 8$, we should get $\frac{k'_c}{k_c} = 1\cdot22$, against 1·18 found.

Experimental.

The object was to determine the ratio of carbonate and bicarbonate in a very dilute solution in equilibrium with air containing a known amount of carbonic acid. Preliminary trials showed that a N/80-solution of sodium carbonate reached equilibrium with pure air when about 80 per cent of the base existed as bicarbonate and 20 per cent as carbonate. Ordinary air therefore contained a suitable percentage of carbonic acid. The actual amount of carbonic acid in the air used (drawn from outside the laboratory and washed) was determined by drawing the air in series through N/10- and N/80-solutions of carbonate.

In order to be sure that equilibrium was reached, the check solutions of N/1-strength were placed in some cases both before and after the dilute solution. The temperature was kept at 25° by a Hearson's regulator, and the solutions were agitated by being shaken in flasks (steamed Jena glass) on a small truck running on rails, at the same time that air from outside the laboratory was drawn through them. Special arrangements were made to prevent the liquids passing from one flask to the other. The amount of carbonic acid in the air was calculated from the analysis of the decinormal solutions by McCoy's formula,—

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* *Transactions of the Chemical Society*, cxi., 1917.

$$[H_2CO_3] = \frac{2c}{5300} \cdot \frac{x^2}{1-x},$$

where c is the concentration of the base in equivalents, $100x$ the percentage of bicarbonate in the liquid, and $[H_2CO_3]$ the concentration of the carbonic acid.

For the analysis of the liquid the method of double titration with phenolphthalein and methyl-orange was adopted, with certain precautions.

Küster, Lunge and Lohöffer, and others have thrown grave doubts on the accuracy of this method, alleging that it gives results for the carbonate which may be 3 or 4 per cent too high. Küster attributes this to the supposed considerable alkalinity of bicarbonates to phenolphthalein. McCoy has already shown that the alkalinity of bicarbonates is very small, and Seyler (*Analyst*, 1897, xxii., 314) showed that if loss of carbonic acid is avoided the results are correct to within less than 1 per cent, although usually on the high side. This question is the subject of an investigation by Seyler and Tripp, shortly to be published. It was found that the point of neutrality to this indicator is very close to that required for the bicarbonate. It may be slightly on one side or the other. The end-point depends on the conditions of visibility of the colour, the amount of indicator used, and not only the total sodium concentration, but the ratio of sodium chloride to bicarbonate at the end of the titration. To avoid errors from this source the following precautions were adopted.

Loss of carbonic acid was avoided by titrating in a tall Nessler glass, adding the acid slowly from a burette with a long delivery tube reaching to the bottom of the vessel, and stirring continually with a circular stirrer, which was never lifted above the surface. Under these conditions it was proved that no appreciable loss of carbonic acid occurred even in fairly concentrated solutions.

The amount of indicator was carefully measured, and the colour at the end-point compared with a check experiment. Other influences were allowed for as follows:—

A check experiment was conducted with each determination, in which the conditions were the same as regards concentration of bicarbonate and sodium chloride.

A standard solution (usually N/10 or N/20) of sodium carbonate in boiled neutral distilled water was prepared and kept out of contact with carbonic acid.

The standard hydrochloric acid was made with boiled water and acid, and protected. An equivalent solution of neutral sodium chloride was prepared and protected.

A preliminary titration was made with phenolphthalein and methyl-orange on the liquid to be analysed.

Let x be the number of cc. of acid required with phenolphthalein.

Let m be the number of cc. of acid required with methyl-orange. A comparison tube with the same amount of indicator and an equal volume of water saturated with carbonic acid was used to judge the end-point.

The standard employed was $2(m-x)$ cc. of carbonate diluted to a given volume, and very carefully titrated with phenolphthalein. This was used as a comparison cylinder in the titration of the liquid to be analysed. The final condition in the standard is:—

Sodium bicarbonate, $m-x$ cc.
Sodium chloride $(m-x)$ cc. (produced in the titration).

The point of theoretical neutrality is $m-x$. If the titration differs from this by, say, y cc., then y is the correction to be applied to the titration.

To the liquid to be analysed is added $m-2x$ cc. of the salt solution. At the end of the titration the conditions will therefore be:—

$m-2x$ cc. bicarbonate pre existing.
x cc. formed from carbonate in titration. Final carbonate, $m-x$.
Sodium chloride, $m-2x$ added
x formed by titration.
Total at the end of titration, $m-x$.

In both standard and assay there are thus the same amounts of bicarbonate and chloride diluted to the same volume.

When the experimental liquid contained sodium chloride this was added to the standard to make the final amount the same.

Example.

Preliminary titration, 10 cc. required $m = 20·21$ cc. N/20-acid.
$x = 5·94$

Standard, $2(m-x)$ .. .. = 28·54
True bicarbonate, $m-x$ .. = 14·27
Required to phenolphthalein 14·11

y = 0·16

This has to be added to the titration to get the true result.

Final titration, $m = 20·21$
$x = 5·83$
$m - 2x = 8·4 =$ salt added.

Corrected figure for x, 5·83 + 0·16 = 5·99.

10 cc. contain .. .. 20·21 N/20 total base
Carbonate, 2 × 5·99 .. = 11·98

Bicarbonate .. .. = 8·23

Carbonate, 40·7 per cent.
Bicarbonate, 59·3 per cent.

Example 2.

Preliminary titration, 50 cc. required $m = 12·58$ cc. N/20-acid.
$x = 1·23$

Standard . .. . 22·7 cc. = $2(m-x)$
11·35 $m-x$
Required to indicator .. .. 11·14

Correction .. .. 0·21 to be added

Final titration, $m = 12·58$
$x = 1·14$

True value of $x = 1·14 + 0·21 = 1·35$.

Total base on 50 cc. = 12·58 N/20
Carbonate, 2 × 1·35 = 2·70

Bicarbonate .. .. 9·88

Carbonate, 21·5 per cent.
Bicarbonate, 78·5 per cent.

Results of Experiments.

Temp. 25°. c.	Bicarbonate $100x$.	Carbonate $100(1-x)$.	$[H_2CO_3]$.	k_c.
101·025 × 10⁻³	42·18	57·82	0·01173 × 10⁻³	5300
12·55	80·51	19·49	0·01173	7130
12·627	80·63	19·37	0·01173	7228
100·8	40·47	59·53	0·01046	5300
100·5	40·60	59·40	0·01052	5300
12·58	78·53	21·47	0·01049	6892
101·05	40·72	59·28	0·01066	5300
100·50	40·89	59·11	0·01072	5300
12·45	79·60	20·40	0·01069	7233

We have, then, for $c = 12·5 \times 10^{-3}$:—

k_c.
7134
7228
6892
7233

Mean .. 7124

Table A.—*Effect of Sodium Chloride.*

Concentration of base as carbonates.	Concentration of sodium chloride.	Total sodium concentration.	100x.	100 (1 − x).	[H_2CO_3].	k_c.
100·00 $\times 10^{-3}$	—	100·0	40·83	59·17	0·01035	—
100·00	—	100·0	40·61	59·39	0·01220	—
100·00	900·0	1000·0	36·40	63·60	0·01035	3869
100·00	900·0	1000·0	36·10	63·90	0·01022	3836
12·58	—	12·580	78·53	21·47	0·01490	6892
12·04	87·5	99·54	77·24	22·76	0·01035	6100
12·00	87·5	99·50	77·83	22·17	0·01022	6417

Table B.

Temperature (°).	c_2.	c.	kk_d.	k.	k_d.
25·1	4·935 $\times 10^{-2}$	49·871 $\times 10^{-2}$	8·45 $\times 10^{-4}$	6·658	12·69 $\times 10^{-5}$
25·1	4·975	37·765	8·09	6·658	12·15
25·1	4·950	23·400	7·81	6·658	11·73
25·0	4·925	23·750	8·37	6·608	12·67

Table C.

25·00	6·360 $\times 10^{-3}$	246·80 $\times 10^{-3}$	14·72 $\times 10^{-4}$	6·608	22·2 $\times 10^{-5}$
24·95	6·183	253·20	14·52	6·633	22·9
25·10	5·820	182·65	14·24	6·658	21·4
24·95	6·010	194·40	11·18	6·633	16·8
24·95	6·075	191·95	10·80	6·633	16·3

We put on record some experiments with N/150- and N/200-solutions, although here the titration with phenolphthalein is so small that the correction becomes comparable in magnitude with it.

However, they were very carefully made by the same method :—

c.	100x.	100 (1 − x).	[H_2CO_3].	k_c.
6·800 $\times 10^{-3}$	87·84	12·16	0·01102 $\times 10^{-3}$	7830
6·540	87·48	12·50	0·01100	7270
4·870	89·80	10·20	0·01173	6468
4·872	90·22	9·78	0·01173	6920
4·410	90·24	9·76	0·01100	6680
5·300	88·65	11·35	0·01100	6697

The average of these is 7123, identical with that for N/80-solutions.

Even at N/200 the concentration of the hydroxyl ion is too small to affect the results materially.

$$[OH] = 1{\cdot}95 \times 10^{-4}\ \frac{[CO_3]}{[H_2CO_3]} = \frac{1{\cdot}95 \times 0{\cdot}25}{5} \times 10^{-4} =$$
$$= 0{\cdot}0097 \times 10^{-3}.$$

This is still not large compared with 0·50 $\times 10^{-3}$ equivalents of base as carbonate, or 4·5 $\times 10^{-3}$ equivalents of bicarbonate. (Table A).

Hydrolysis of Sodium Carbonate by Hydrolysis of Ethyl Acetate.

Shields' method was followed. The symbols have the following meaning :—

c = original concentration of the ethyl acetate in the mixture.
c_2 = original concentration of the sodium carbonate in the mixture.
x = number of grm.-molecules of carbonate changed to bicarbonate.
t = time in minutes.
k = velocity-constant of hydrolysis of ethyl acetate.

About 200 cc. of the sodium carbonate solution (made with boiled distilled water) were mixed with 200 cc. of a solution of neutral ethyl acetate of known strength. The initial time was taken as halfway between the beginning and end of the mixing of the solutions, and the final time the beginning of the titration ; 20 to 50 cc. were withdrawn from time to time, and titrated with N/20- or N/40-hydrochloric acid. The titration was made with the usual precautions to a very faint pink with phenolphthalein. The temperature was about 25°, the solutions being maintained at that temperature before mixing.

The value of k was obtained by the formula—

$$(3{\cdot}132 + k)(4472 - T) = 192{\cdot}07,$$

which was found to represent the values given by Shields in the neighbourhood of 25°. Thus at 25° we have $k = 6{\cdot}608$ (Goldschmidt, *Ber.*, 1899, xxxii., 3396, gives 6·94 at 25°).

The value of k_d is found from the formula—

$$t.kk_d = \frac{c_2}{c - c_2} \log_e \frac{c_2}{c_2 - x_1} - \frac{c}{c - c_2} \log_e \frac{c}{c - x_1}.$$

We give the full experimental data in three typical cases.

N/10-*Sodium Carbonate.*

Conditions similar to those of Shields. Temperature, 25·1°.

t.	$c_3 - x$.	x.	$c - x$.	kk_d.
0	4·935 $\times 10^{-2}$	—	49·871 $\times 10^{-2}$	—
10	3·160	1·775	48·096	8·736 $\times 10^{-4}$
15	2·875	2·060	47·811	8·340
20	2·635	2·300	47·571	8·250
30	2·285	2·650	47·221	7·990
40	2·000	2·935	46·936	7·970

Average, $kk_d = 8{\cdot}45 \times 10^{-4}$.

The results obtained are given in Table B.

N/10-*Sodium Carbonate.*

In these experiments a correction was applied to the results to allow for the effect of the sodium acetate formed on titration. This was made by partly neutralising a similar solution to that being titrated by acetic acid, and comparing the hydrochloric acid required to complete the titration with the carbonate actually present. Thus, in the absence of acetate the carbonate was correctly estimated at 12·95 $\times 10^{-3}$.

When the acetate was 8·38 $\times 10^{-3}$ and the carbonate 4·57 $\times 10^{-3}$, 4·67 cc. of acid were required, an excess of 0·1 cc.

When the acetate was 11·52 and the carbonate 1·43, 1·57 cc. of hydrochloric acid were required, an excess of 0·14 cc. By graphic means the value of this correction was found for each titration, and the corresponding reduction made.

Temperature, 25°; 200 cc. of N/40-carbonate mixed with 200 cc. of ethyl acetate solution ($c = 493{\cdot}6 \times 10^{-3}$).

50 cc. withdrawn and titrated with N/40-acid.

t.	$c_3 - x$.	x.	$c - x$.	kk_d.
—	$6{\cdot}3600 \times 10^{-3}$	—	$246{\cdot}80 \times 10^{-3}$	—
10·00	1·6860	4·674	242·13	$15{\cdot}52 \times 10^{-4}$
14·75	1·2820	5·078	241·73	14·15
20·00	0·8780	5·482	241·32	14·60
30·00	0·4739	5·886	240·92	14·62

Mean, $kk_d = 14{\cdot}72 \times 10^{-4}$.

Experiments conducted in this way are given in Table C. Two experiments gave lower results, but we could see no reason for excluding them.

It is possible that these lower results are due to the highly dilute solutions having accidentally absorbed some carbonic acid. If B is the concentration of the bicarbonate originally present in the solution then the formula becomes—

$$k.k_d.t = \frac{B + c_2}{c - c_2} \log_e \frac{c_2}{c_2 - x} - \frac{B + c}{c - c_2} \log_e \frac{c}{c - x}.$$

N/200 temperature ..	25°
c_2	$2{\cdot}5 \times 10^{-3}$
c	$90{\cdot}8 \times 10^{-3}$
kk_d	$15{\cdot}2 \times 10^{-4}$
k	6·608
k_d	$23{\cdot}0 \times 10^{-5}$

Conclusions.—1. The apparent variations of the second ionisation constant of carbonic acid in the equilibrium equation $[H] \times [CO_3] = k_3[HCO_3]$ are due to the ionisation of the sodium bicarbonate (α) and that of sodium carbonate (β).

The variation of the hydrolysis constant of sodium carbonate, $k_d = \frac{k_w}{k_3} \frac{\beta}{\alpha}$, in Shields' experiments, and of $k_c = \frac{k_2}{k_3} \frac{\beta}{\alpha^2}$, in McCoy's experiments, is due to the same cause.

2. By experiments at high dilutions, the value of k_3 at 25° has been estimated at $4{\cdot}27 \times 10^{-11}$, and $\frac{k_w}{k_3} = 19{\cdot}2 \times 10^{-5}$, $\frac{k_2}{k_3} = 7124$.

3. The value of α, the ionisation of sodium bicarbonate, either alone or in presence of sodium chloride or carbonate, may be taken as equal to that of sodium acetate at the same molecular concentration.

4. The value of β, the ionisation of sodium carbonate (in respect to the CO_3 ion), between equivalent concentrations 1000×10^{-3} and 100×10^{-3} (and probably at higher dilutions) may be approximately represented by the empirical formula $\beta = 1{\cdot}104 - 0{\cdot}320 \log c$, where c is the sodium concentration in mgrm.-equivalents per litre.

5. In the presence of sodium chloride the apparent value of β is greater than for pure bicarbonate and carbonate solutions at the same sodium concentration.

If r is the ratio of sodium as chloride to sodium as bicarbonate and carbonate, then—

$$\beta = (1{\cdot}104 - 0{\cdot}320 \log c) . \frac{1 - 0{\cdot}1512 \log (r+1)}{1 - 0{\cdot}3096 \log (r+1)}.$$

These values are considerably less than those estimated on the usual assumptions from conductivity of the analogous salt, sodium sulphate, but they represent the "active mass" of the sodium carbonate molecule at the given concentration, and probably the concentration of the CO_3 ion.

6. It is confirmed that the ionisation of sodium carbonate takes place in two stages, namely, $Na_2CO_3 = Na + NaCO_3$ and $NaCO_3 = Na + CO_3$.

The value of the second ionisation "constant," $k_b = \frac{[Na] \times [CO_3]}{[NaCO_3]}$ calculated, and shown to be smaller and more constant than is the first.

(To be continued).

A NOTE ON THE CAUSE OF THE PINK COLOUR OBSERVED IN CERTAIN HYPOCHLORITE BLEACHING SOLUTIONS.

By H. G. ELLEDGE.

When sodium hypochlorite bleaching solutions are prepared for use in laundering, by treating a solution of calcium hypochlorite, or bleaching powder, with a solution of the so-called neutral washing powder (see Note) after the calcium carbonate had settled out, a pink coloured solution invariably appears. This coloration has been observed when various trade brands of bleaching powder were employed, some of which were of American manufacture and others of English origin; in fact, it seems to result in every case where an excess of the HCO_3 ion is present in the solution. When bleaching solutions were made of the same bleaching powders, but, instead of the "washing sodas" mentioned, soda-ash or sodium sulphate was used to precipitate the calcium, the colour of the resulting solution was green. By agitating this green solution with sodium bicarbonate, the pink colour was again obtained.

(Note.—These sodas are usually of about the following composition: normal sodium carbonate, 46·3 to 36·1 per cent; sodium bicarbonate, 37·7 to 50·0 per cent; and water, 16·0 to 13 per cent—see Faragher, *Journ. Indus. Eng. Chem.*, 1914, vi., 641. The observations of Faragher have been confirmed and extended by the writer).

When certain laundries adopted soda ash as the wash-room alkali, the wash-room help thereof were concerned about the absence of the pink colour which, through habit and also because of the influence of the sales agents of certain alkali companies, they had come to regard as an index to the bleaching qualities of the solution. Owing to this condition, the writer was requested by the Allegheny County Laundrymen's Exchange to explain the origin of the coloration, and to ascertain definitely whether there was any difference in the bleaching properties of the green and pink solutions. As was to be expected, it was found that equal volumes of the solutions, when made up with identical weights of the same bleaching powder, gave the same values for available chlorine. Among others, bleaching tests on hemp strings indicated that one solution was as satisfactory as the other for laundry bleaching.

The writer was led to conclude that the colour of the pink solution was attributable to the presence of traces of sodium permanganate, the manganese being derived from the bleaching powders used. This conclusion was reached after certain experimental work, of which the following is illustrative: There were made up two solutions of sodium hypochlorite of the same strength. (The solutions were prepared by making a paste of 10 grms. of bleaching powder and water, adding thereto 10 grms. of soda-ash, and, after thoroughly shaking in a flask, making the volume up to 250 cc. This is the strength usually adopted in the laundry for stock solutions). To one of them a small amount of manganous sulphate was added; this produced no change in colour. Then to each of the solutions 10 grms. of sodium bicarbonate were added; after thoroughly shaking and settling, the solutions both assumed a pink colour, but the one to which the manganous sulphate had been added possessed a much more intense colour. By colour comparisons it was estimated that 0·02 per cent to

0·04 per cent of manganese in the bleaching powders would be sufficient to produce this colour.

It was early suggested that the pink coloration might be caused by the presence of small amounts of sodium ferrate. Therefore solutions were prepared as above, and to one of them ferric chloride was added; then to both solutions sodium bicarbonate was added as above. After the precipitates had settled no difference could be observed in the intensities of the pink colour of the different solutions. These and other experiments led to the conclusion that the colour was due to traces of manganese, which, by the catalytic action of the bicarbonate on the hypochlorite, was oxidised to the permanganate, and that, for laundry purposes, this coloration was of no consequence.

Subsequently, when the writer's report became available (the conclusions were reported by bulletin to the Allegheny Country Laundrymen's Exchange on April 17, 1916), the contention was made by a representative of one of the prominent alkali manufacturers that the pink colour was due not to the presence of permanganate, but of a ferrate; and in order to settle definitely the whole matter, the absorption spectrum of the pink bleaching solution was compared with that of a solution of potassium permanganate of the same colour intensity. The solution used was made four times the concentration usually employed, and, after all the precipitate had settled, a saccharimeter tube was filled with the clear pink solution. (The solution of sodium hypochlorite was prepared with 40 grms. of commercial calcium hypochlorite, 40 grms. of soda-ash, and 40 grms. of sodium bicarbonate, made up to a volume of 250 cc. with distilled water). A similar tube was filled with potassium permanganate solution of same colour intensity and the absorption spectra were compared; they were found to be identical. To compare the two more carefully, the two absorption spectra were brought in view at one time, by means of the comparison mirror, and the positions of the lines were shown to be exactly the same.

No attempt is made here to account for the presence of the trace of manganese in the bleaching powder, but the writer feels that he has offered positive evidence that the colour of the pink bleaching solutions is due to the presence of sodium permanganate, and not of sodium ferrate, as some have maintained.—*Journal of Industrial and Engineering Chemistry*, viii., No. 9.

RECENT CHEMICAL DEVELOPMENTS.

War Chemistry in Germany; Increased Gasoline Production.

By ELLWOOD HENDRICK.

Fixing nitrogen from the air to make explosives was an accomplished fact in Germany, and in successful operation before the war was declared. But certain foods called proteins, needed by man and beast, also contained nitrogen although they cannot be prepared in this way. The government food control looked after human needs in a measure, but it could not provide fodder for horses and cattle of a sort containing nitrogen in the right place to keep them going. Five hundred thousand tons of such fodder was annually imported before the war. The need has finally been met by the discovery of a special yeast plant which has a very vigorous growth but produces no alcohol. Under the direction of the Brewers' Institute of Berlin enormous tanks have been set up with proper temperature control and the refuse from the beet sugar works is let into them. Suitable salts are added, including those of ammonium, produced from the air, and these contain the required nitrogen in combination to feed the yeast, which is said to grow with amazing rapidity. When compressed it is reported to serve as an excellent nitrogenous fodder and also to be available for human food. The German scientific papers, from which the *Journal of the Society of Chemical Industry* gathered this information, declare that this will make Germany independent in the future in regard to its supply of nitrogenous feed for horses and cattle.

Another requirement which has been but partially met is oils and fats. The ravages of tuberculosis are in part due to short rations of fats, but the demands of the German war department for munitions containing nitro-glycerin have aggravated this need. To make nitro-glycerin glycerin is necessary, and the glycerin is obtained by treating fats with a caustic alkali, which results in soap and glycerin. This is explained by the fact that fats are combinations of fatty acids and glycerin, and by boiling with an alkali soap is produced which is a combination of fatty acids with an alkali while the glycerin is set free. So far chemists have not been able to produce glycerin in any other way than by starting with fats. So, by rigid command, all kitchen refuse containing fats is delivered at a central station where a proportionate amount of soap is returned to the householder and the glycerin is kept for government use.

There is still a great shortage of fats from the lack of imports of provisions, but it has been discovered that horse chestnuts are rich in oil, and these are now collected and the oil pressed from them. It is not mentioned whether the oil is edible or not, but it seems to furnish a considerable quantity of glycerin and soap. A little more oil has been obtained by collecting cherry pits by the women of South Germany. The pits are crushed and thrown into a salt solution of such specific gravity that the kernels float on the top while the shells sink. The kernels are then skimmed off and pressed for the oil.

Had the Germans cultivated the very prolific soya bean before the war they would have been much better off now. These beans contain 40 per cent of edible protein and 20 per cent of oil, which, on treatment with hydrogen in the presence of nickel, may be changed into a high grade of lard. This is the same method largely used in this country to produce lard substitutes or shortening from cottonseed, peanut, and other oils.

The Gasoline Situation.

The director of the U.S. Bureau of Mines, Dr. V. H. Manning, made an address to the editors of business publications at their conference in Washington on the present situation in regard to gasoline. It was interesting and full of information; but it does not give us a clear idea as to what the price of gasoline is likely to be next year or the year after. We still have the chance to do all the guessing we want to. One big fact that we have to face is that the production of automobiles has increased 200 per cent above the increase in gasoline production. Thus the total gasoline engine horse-power built and sold in the United States in 1913 was 11,200,000, and in 1915 it was 22,500,000. Of course, this rate of increase cannot keep up, but who knows what it will be? Between 55 and 60 per cent of the gasoline produced is used in automobiles, 20 to 25 per cent is exported, and the rest is used in stationary engines, motor boats, and for other purposes. Now leaving out of consideration the increased demands for war, there are the constantly improved highways which make motor trucking the natural method of transportation over them. All of our fishing fleets have installed gasoline power, and even if the demand for pleasure craft and vehicles should decrease the industrial requirements is likely to go up in proportion.

In 1916 there were produced in the United States 295,000,000 barrels of crude petroleum. The stock on hand at the beginning of the year was 175,000,000 barrels, and at the end 150,000,000 barrels, which means that 25,000,000 more barrels of crude petroleum were sold than were produced. As things are going now, unless new supplies are opened up, 1917 will cut down the supply on hand from 150,000,000 to 90,000,000 barrels by the end of the year, besides taking all that is produced.

Now crude petroleum is a very mixed product. It contains varying amounts of gasoline, and when this is all distilled off there is not any more gasoline left in it. But despite this fact we really do get more gasoline out of it by what is known as cracking. After the gasoline is distilled off the heavier oils come over, such as kerosene, export oil, and the various grades of fuel oils, as they are known to the market. The valuable lubricating oils are set aside and treated separately. When the heavier and cheap oils are treated by heat and pressure under special conditions and occasionally with certain reagents, they are, as has been said, chemically knocked to pieces, and some of the pieces are gasoline. This is "cracking," The residues may be cracked again, and then a third time with decreasing results, but after that they are likely to go back to their original elements, carbon and hydrogen; in other words, to coke. Last year this method furnished 7½ per cent of the gasoline used in this country. Some chemical engineers have such faith in cracking that they believe it will give us enough despite all the danger signals. Among the uncertain factors, however, is the endurance of the present wells and the discovery of new ones.

Another source of gasoline supply is natural gas, from which, by cooling and absorption, the very light liquids are separated. This is known as "casing head" gasoline and it is so light that it is mixed with heavier oils like kerosene to make motor fuels. It produced 120,000,000 gals. of fuel last year.

So we can argue both ways about the future of gasoline. There are the possibilities of new supplies, of more from natural gas and the certainty of much more from cracking. On the other hand, there is the decreasing supply in storage, which is more convincing than argument or oratory. And the demand for motor fuel is growing like a green bay tree, very, very much faster than the petroleum supply is growing, and cracking is not yet a perfect art. It looks as though we had not yet got past the worrying stage in regard to the gasoline supply.—*Scientific American*, June 16, 1917.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

By IRVING LANGMUIR.

(Continued from p. 56).

Crystal Structure from the View Point of Chemical Theory.—The work that has been done so far on crystal structure testifies to the general applicability of such theories of chemical constitution as that of Werner.

Except in the case of diamond crystals, no structural formula can be written consistent with our ordinary ideas of (primary) valence, which adequately represents the constitution of the crystal. We see, however, that the arrangement of the atoms in crystals is just what we should expect if the forces binding the atoms together are similar to those forces which, by Werner's theory, must hold together the *molecules* in molecular compounds (compounds of higher orders).

Werner's theory, however, needs to be modified in some respects, to fit in with the new work. According to Werner, compounds of the first order are held together by primary valence, and only when these simple compounds form compounds of higher orders are the residual valences called into play. But when we consider the structure of the halide salts of the alkalis and the structure of such crystals as fluorite, we must conclude that even in the case of these first order compounds the ordinary rules of valence do not always apply.

It thus seems that secondary, or residual, valence is active, not only in the higher order compounds, but that a valency of the secondary type may also characterise single atoms when these are combined with others in crystals.

It is evident that solid bodies could not be built up of atoms held together exclusively by primary valences except in the case of atoms having valences of four or more. Thus, when two monovalent atoms combine to form a gas molecule, they are held together by primary valence. If there were no residual valence, these molecules could not condense either as a solid or liquid. Divalent atoms could combine together in long chains, but these chains could not be linked together except by secondary valence. With trivalent atoms branching chains could be formed which could interlock so as to cover a plane surface, but except by secondary valence no atoms could be held outside of this plane. With tetravalent atoms, on the other hand, the atoms can be linked together by their primary valences, as in the diamond crystal, so as to fill a volume.

We thus see that primary valences cannot play an important part in crystal structure in the case of atoms with a valency of less than four. Most of the crystals containing tetravalent atoms which have been studied so far, have shown that the primary valences of the tetravalent atoms seem to exert their influence. This is shown not only in the case of the diamond, but in zircon, cassiterite, and rutile, in which each atom of Zr, Si, Ti, or Sn is clearly associated with two atoms of oxygen.

From these considerations it seems that in general there is a strong tendency for every atom to form compounds by means of its primary valence, but where the conditions are such that combination by primary valence is no longer possible, then secondary valence is called into play and may entirely supersede the primary valence.

Thus, when sodium atoms and chlorine atoms combine at high temperatures to form gaseous NaCl, the primary valence holds the atoms together. But when the pressure is raised or the temperature is lowered, the secondary valence is enabled to completely supersede the primary valence, since the primary valence cannot cause the combination of the molecules necessary to form a solid body.

With divalent and trivalent atoms a sort of divided valence like that suggested by J. J. Thomson is apparently often manifest, and is probably a sort of transition between primary and secondary valence. This is seen particularly in crystals of the spinel group, in which the divalent atoms have assumed a tetravalent character and the trivalent atoms a hexavalent character.

By this division of each of the valence units into two parts, the apparent valency is raised to four or more, so that the solid body can then be held together by this means. According to Stark and J. J. Thomson's theories, we should never expect the subdivision of a primary valence unit into more than two parts. Furthermore, we should not expect that a monovalent element would often exhibit this divided valence in solid bodies, because even if its apparent valence was doubled by this means, it still would not be able to make use of this valence in forming a crystal.

The compounds whose crystal structures have been studied thus far are all more or less of the polar type. It is not safe to conclude that the structures of nonpolar compounds will be similar to those already found.

For example, when an organic compound such as methane is crystallised as a solid and is then converted again into a gas, it is certain from chemical considerations, that none of the hydrogen atoms have been separated from the carbon atoms to which they were originally attached. The identity of the original molecules must, in a sense, have been preserved even when the methane was in the solid condition.

On the other hand, with crystals of the types studied so far, the substance could not be condensed from the gaseous condition and be re-evaporated again without most of the atoms having exchanged partners. Thus, when a crystal of sodium chloride evaporates, a sodium atom on the surface may escape with any one of the four adjacent chlorine atoms as a molecule of salt vapour. There is only a small chance that the particular chlorine atom with which it escapes will be the same one as that with which the sodium atom was combined before it formed part of the crystal.

From these considerations we are forced to conclude that in crystals of methane each carbon atom is surrounded by four hydrogen atoms held to it by primary valences. The crystal is then held together by residual valences. Since the methane is so thoroughly saturated chemically, these residual forces are very weak and, therefore, methane melts and boils at a very low temperature. But there is absolutely no reason for assuming that these residual forces are any less chemical in nature than those which cause the combination of K_2O and SO_3 to form K_2SO_4, We certainly cannot limit chemistry to a study of only those substances whose atoms are held together by primary valence.

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* From the *Journal of the American Chemical Society*, xxxviii., No. 11.

Determination of the crystal structure of organic compounds should prove of very great value in clearing up the true distinctions between primary and secondary valence. Unfortunately the very low absorption of X-rays by the hydrogen makes it difficult to determine the positions of the atoms of this element by the present methods. This difficulty can be avoided by choosing such substances as C_2Cl_6 and C_6Cl_6.

Similar considerations to those used with methane apply to such substances as H_2, N_2, O_2, &c., and nearly all typical organic substances. That the crystal structure, even with these substances, depends on the space arrangement of the atoms, is clear from the work of W. Wahl (*Proc. Roy. Soc.*, A, 1913, lxxxviii., 354) on the crystal forms of the lower members of the aliphatic hydrocarbon series. He finds methane crystallises in the isometric system, ethane in the hexagonal, propane apparently rhombic, trimethyl methane probably rhombic. Tetramethyl methane occurs in two modifications, one isometric and one tetragonal. Normal butane also has two forms, hexagonal and rhombic. Normal pentane is rhombic, while normal hexane, heptane, and octane are monoclinic or triclinic.

The lower members of this series show a remarkable agreement between the chemical constitution and the crystal form. Thus the symmetry of the methane molecule requires a crystal of the isometric form, probably with an arrangement rather similar to that of the diamond. If we look upon the carbon atom as having its bonds arranged symmetrically after the pattern of the tetrahedron, then the ethane molecule would consist of two carbon atoms each with three hydrogen atoms (in planes 120° apart) arranged around them. This leads naturally to the hexagonal form.

The definiteness of this dependence of the crystalline form upon the arrangement of the atoms indicates that even with these nonpolar compounds the forces holding the *molecules* together in the crystals are of the same nature as those holding the *atoms* together in the polar types of crystals.

Since the forces acting between the molecules in these crystals are then quite similar to those acting in the more complex inorganic compounds, we would still be justified in regarding a crystal of methane as one large molecule. We thus have molecules within the molecule.

This leads us to consider whether it is not desirable to revise our conception of the molecule. There is an advantage in looking upon every crystal (and in fact every mass of liquid) as a single large molecule, in that this viewpoint brings out strongly the *chemical* nature of the forces holding the crystal together, and thus encourages us to apply to the study of these forces the knowledge already available from other fields of chemistry.

On the other hand, there is a real need for a term to denote a group of atoms which can pass from the gas phase to the solid (or liquid) and back again without the exchange of any atoms. If, however, we should limit the word molecule (in liquids and solids) to this narrow definition, we would have to say that there are no molecules at all in the great majority of inorganic substances.

On the whole, it seems best to define a molecule as *a group of atoms held together by atomic forces.* We must then distinguish between various kinds of molecules.

The *gas molecule* may be defined in terms of Avogadro's Law, and is thus only sharply definable in so far as the gas follows the laws of ideal gases. We may define a *fixed molecule* as the largest aggregate of atoms which may pass from the gaseous phase to the solid (or liquid) phase and back again to the gaseous phase without exchange of atoms with other aggregates. With substances which are wholly nonpolar, such as the saturated hydrocarbons, this definition of fixed molecule is probably never ambiguous. But with molecules which are partly polar, as, for example, acetic acid, this definition may lack sharpness. Thus, when CH_3COOH vapour dissolves in water (or condenses as a solid), it is probable that the replaceable hydrogen atom will be exchanged with that of the other CH_3COO groups. According to our definition of fixed molecule we must, therefore, consider that the *fixed molecules* in liquid or solid acetic acid consist of CH_3COOH groups. Cases will frequently arise, as, for example, in the alcohols, where the rate of exchange of the hydrogen atoms is so slow as to be almost negligible, so that it will be impossible to limit sharply the extent of the fixed molecule. This dificulty, however, seems an inherent one, for it depends upon the fact that all possible degrees of tautomerism may actually exist in the large molecule forming the whole mass of the solid or liquid.

It will also be convenient to distinguish another type of molecule which we may call the *group molecule.* This may be defined as an aggregate of atoms which are interrelated in such a way (by position or mobility) that the atoms in the group may be distinguished from atoms outside the group. Thus in solid methane each hydrogen atom is associated with a particular carbon atom, while the carbon atom is associated with four hydrogen atoms. All other hydrogen atoms beside these four may be distinguished from these by their being combined with a different carbon atom.

If we represent a methane crystal diagrammatically as follows—

$$\begin{array}{ccc} H & H & H \\ HCH & HCH & HCH \\ H & H & H \\ H & H & H \\ HCH & HCH & HCH \\ H & H & H \end{array}$$

it is evident that we might also look upon the crystal as consisting of group molecules of hydrogen (H_2) held together by carbon atoms. Chemical considerations, however, would lead us to choose CH_4 as the group molecule.

In liquid methane we could distinguish the group molecule either by the fact that four atoms of hydrogen must be geometrically associated with a single carbon atom, or by the fact that four hydrogen atoms always move with a particular carbon atom, whereas all other neighbouring hydrogen atoms in the course of time gradually (by diffusion) become separated more and more from the given carbon atom.

A crystal of zircon would thus be a compound consisting of group molecules of ZrO_2 and group molecules of SiO_2.

In inorganic compounds in the solid or liquid state there are usually no fixed or group molecules. It is probable, however, that an ion of the type CO_3^{--} in solution constitutes a group molecule, since the structure of the calcite crystal suggests the carbon atom may be more or less permanently associated with three particular oxygen atoms. An ion of the type OH^-, however, can probably not be properly looked upon as a group molecule since the high mobility of the OH^- ion and other factors indicate that this ion is continually exchanging its atoms with the surrounding mass of water.

Besides these types of molecules, there are the large molecules which constitute colloid particles. These may be called *colloid molecules.* They probably usually consist of large aggregates of atoms or group molecules combined together by means of secondary valence. In the second part of this paper the probable structure of these colloid molecules will be discussed in more detail.

Finally, every continuous solid or liquid mass, whether homogeneous or not, may be looked upon as consisting of one large molecule. We may speak of molecules of this type as *solid* or *liquid molecules*.

(To be continued).

SHALL GREAT BRITAIN AND AMERICA ADOPT THE METRIC SYSTEM?[*]

(Concluded from p. 57).

The President (Mr. Edgar Taylor) said he would call upon Mr. Harry Allcock, the author of a most valuable lecture delivered recently before several kindred institutions, to open the discussion against the arguments used by the author. Mr. Allcock had kindly come down specially from Manchester to favour them with his views.

Mr. Harry Allcock said that before dealing with the contents of the paper he would like to say that he was the victim of two disappointments. In the first place he had hoped to be able to join with the members in welcoming Mr. Ingalls to a meeting of British mining engineers. Mr. Ingalls was a gentleman of very considerable eminence and attainments in America, and it was accordingly all the more to be regretted by many of those present that, in his capacity as president of the American Institute of Weights and Measures, he had accepted a broom with which he apparently hoped to stem the metric tide. The metric tide was approaching the full, and it would be very much to be deplored if a gentleman of Mr. Ingalls' parts were to be swept off his feet by that tide. Again, he had wanted to meet Mr. Ingalls so that he might have the benefit of one of those after-meeting conversations with him over their coffee, which were frequently so very much more interesting because all formalities were broken down, and to hear from him what his objections really were, because to his mind none of those advanced in the paper was insuperable.

Then he had had a further disappointment, in that owing to an unfortunate misdirection he had been unable to reach the meeting in time to hear the first part of the remarks of the gentleman who had opened the discussion in Mr. Ingalls' unavoidable absence. With his permission, he would therefore leave that gentleman's remarks to be dealt with by subsequent speakers, and would devote himself to the arguments advanced in Mr. Ingalls' paper, a copy of which the secretary had been kind enough to send him.

Reviewing those arguments one found several admissions which, when followed to their logical conclusion, provided striking testimony in favour of the reforms which the author had set out to oppose. For instance, although America and the United Kingdom were claimed to be strong adherents of what was honoured by the name of the Imperial System (?) of Weights and Measures, they had the author's admissions, in his introductory note and elsewhere in his paper, that the application and practice of that so-called system differed in those two countries.

When they added to that the statement made by the late Sir William Preece in 1903 that we employed 154 different units of length, and the further fact quoted in the House of Commons by Sir Henry Norman in 1907 that we employed 200 different weights and measures in the British corn trade alone, one could quite appreciate the author's further admission that reform was urgently necessary.

Now along what lines should such reform be attempted? The author said on p. 1, "The advantages of the decimal system are manifest," and on p. 2 he said "The idea of establishing uniformity is in itself alluring."

They must all admit that our adoption of the Metric System would secure for us both these advantages, in addition to others incidental to that system. On the other hand, if we followed the author's advice and decimalised our existing units of weights and measures we should thereby accept all such difficulties as were incidental to any change, and in the end find ourselves in the possession of an inherently bad system because of the absence of correlation between our units of length, weight, volume, and area.

On that question he might perhaps refer to the recommendations of a Select Committee of the House of Commons so long ago as 1862, which reported in these words: "It would involve almost as much difficulty to create a separate decimal system of our own as simply to adopt the Metric System in common with other nations. And if we did so create a national system, we would, in all likelihood, have to change it again in a few years, as the commerce and intercourse between nations increased, into an international one."

That was fifty-five years ago, and if the Committee of the House of Commons, with the information then available, anticipated the possibilities of a further change when the volume of international trade had developed sufficiently, what would they have said under the present conditions of enormously increased international trade, and what therefore ought we to say on the same problem? It must also be recognised that if we proceeded along the alluring path of decimalising the pound, the gallon, and the yard and so forth, we should remain as far off as ever from the ideal of uniformity with other nations.

Before leaving the question of correlation between units he would like again to refer to the paper. The author said on p. 8 in regard to correlation: "It may freely be admitted that there is some merit in this," and again on p. 11: "The Metric System has many good points, chief of which is the correlation among measures of length, area, volume, and weight."

On the question of uniformity the author suggested—he could not think seriously—that if uniformity was so desirable, why did we not go into the metric countries and ask them to accept the English units? Well, metric advocates realised some of the difficulties of bringing about any change even when they had on their side all the arguments, all the scientific structure of the Metric System, and every advanced view in science and industry. If they realised the difficulty, what would the poor fellow do who went into a metric country to urge their adoption of our chaotic and cumbersome jumble of tables which we chose to call a system? He was sure they would all agree that such proposals would be met with ridicule, and ridicule would break the hearts of any such missionaries—if indeed such could be found.

Then it must be remembered that if uniformity was desirable—and he thought in these days everyone was prepared to admit that it was—it must come down ultimately to the choice of either the Imperial System or the Metric System. No intermediate course was now possible.

Let them also remember that whether we would or not we must use the Metric System to an ever-increasing extent in this country because of our trade with other countries. On the other hand there was no compulsion for us to perpetuate the two systems, which we had been doing for many years past. He supposed that most of those present, either in science or industry or export trade, had had to work partly in the Metric System and partly in the English system, and they would have to continue to work in the two systems until they chose to abandon the less efficient. When one put it in that light he thought they would all agree that the English system was the less efficient and that sooner or later it must go. If it must go sooner or later, then the sooner the better in point of difficulties to be overcome.

In the existing postal system he supposed we had one of the best instances of world-wide international trade, and it was significant that when faced with the necessity of providing schedules of charges for the interchange of mail matter between the different nations of the world it was found necessary to adopt the Metric System as their basis They had found that out over fifty years ago.

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[*] Opening of a Discussion on a Paper by Mr. W. R. Ingalls read before the Institution of Mining and Metallurgy, May 17, 1917 (*Bull.*, No. 152).

On this point he would read a single paragraph from a very excellent book on the "Evolution of the Metric System" (by Messrs. Hallock and Wade, two American gentlemen), which was published in 1906: "The interchange of mail by all the civilised countries of the world represents the most extensive use of a uniform system of weights and measures in the world, and has been carried on for many years without the slightest confusion or embarrassment. All mail matter transported between the United States and the fifty or more nations, signatories of the International Postal Convention, including the United States and Great Britain even, is weighed and paid for entirely by metric weight."

There was another aspect of the subject which he would like members of the institution to consider, viz., that the Metric System had been accepted as the international language of quantity by the scientists of the world, including our own and those of America. This meant that the scientists of America and the United Kingdom calculated and experimented in the Metric System and the manufacturers in these countries adhered to the old Imperial system. That being so, surely it was in our interest to break down the artificial barrier which at present stood between the scientist in his laboratory and the industrialist in his workshop. It would certainly be an advantage that these two classes of brain should be in as close contact as possible.

There had been many exhortations and he might almost say warnings on the part of the Government and others since the war had broken out, that a closer intimacy of contact between these two interdependent sections of the community was necessary for the future welfare of this country. Let us make it easy for them to co-operate and, by our adoption of the Metric System, provide one language of quantity for use throughout the world.

It was noteworthy that the author admitted he found the Metric System exceedingly useful in laboratory work, where he would not think of using any other system. Why admire the principles and value the utilities of the Metric System in laboratory work, and yet at the same time say, "Let us maintain"—for ever, presumably—"the English system in our workshops."

Another point was that he thought the author laid too much stress on the value of what he described as the accumulated knowledge stored in the library of an engineer. The engineering industry—and one might almost say all technical industries—continued to advance so rapidly that they all knew—many of them to their cost—that the literature which was standard even a few years ago was now quite out of date; it was obsolete, it described a practice which was no longer followed; and he thought, on consideration, it would be found that the value of such accumulated knowledge as is expressed in English weights and measures was not so great as the author would have them believe.

It was a sign of the times that many technical societies, engineering institutions, and technical journals had already adopted the practice of placing the metric equivalents alongside all English dimensions. It was an admission that data which they hoped would be of permanent use must be expressed in the Metric System, as otherwise they could not survive more than a few years.

On the question of education, the author had rather surprised him by saying that the scholars with whom he had come in contact had had the greatest difficulty in learning the Metric System. There was surely something wrong about that statement. That was one of the things he had wanted to discuss with the author. He thought he must have meant that some scholars rather disliked the conversion tables they had to learn. They did not learn merely the Metric System; they learnt that one méter equals 39·37 in. instead of one mètre equals 100 centimètres, and it was the 39·37 in. part of the table which terrified them, and not the 100 centimétes. In other words, it was a mixture of the systems which appalled them and not the Metric System itself.

On the question of interference with standards, the author apparently held the view that all existing standards were sacred. Standards were good and valuable, it was true, but it wrong to assume that the standard of to day was likely to be the standard of next year. For instance, our Engineering Standards Committee in their current annual report, recognising the mutability of standards, had published this sentence:—

Revision of reports. Reports have already been issued on many of the subjects referred to above, but it has always been recognised, from the inception of the movement, that, to avoid stereotyping present practice, revisions will from time to time be necessary. To meet this, the main committee has made a ruling that each sectional committee shall be afforded an opportunity of meeting at least once a year to consider whether any revisions in the specifications and reports drafted by it are desirable.

He would very much like to have the author's revised opinion upon the sacredness of standards after his consideration of that paragraph.

Then in regard to the "practical man" argument, the taunt was thrown out against metric advocates that they were all scientists or dreamers or idealists and, in fact, anything but "practical men." If to be a practical man meant merely to be the "horny-handed son of toil," perhaps some of the metric advocates were not practical men; but if that designation included engineers of proved experience then he thought it must be admitted that many such practical men had long since realised the advantages of the Metric System.

For instance, only a few months ago—to quote a case in the author's own country—there was a symposium in New York of all the principal engineering institutions to consider the question of the Metric System, and he was informed they all, with the single exception of the representatives of the mechanical engineers, were in favour of the Metric System. Now, wherein did mechanical engineering differ, for instance, from electrical engineering to-day? Electrical engineers throughout the world were in favour of the Metric System, and it must be admitted that the electrical engineer, with his 20,000 kilowatt generators, and so forth, had to solve big mechanical engineering problems just the same as if he were designing and making steam engines. The modern electrical engineer must, of necessity, be a sound mechanical engineer. Operations were of the same general character to-day in electrical engineering workshops as in mechanical engineering workshops, so that if electrical engineers said: "We desire the adoption of the Metric System and would welcome it," why did not mechanical engineers say the same thing?

The answer presumably was that the electrical industry was a modern industry, going back only about thirty years, and that at the outset, recognising the advantages of the Metric System, it has adopted it as the best system available. If the Metric System had been available when mechanical engineers commenced their operations a century or so ago, he thought there was no doubt whatever that they also would have been metric advocates.

Many people feared that if an Act were passed to render the use of the Metric System compulsory instead of permissive, they would forthwith have to scrap all their valuable stocks of patterns, tools, jigs, gauges, and the like. Such was certainly not intended, and such would not be the case, as was evident from the clause which was incorporated in the draft Metric Bill which was now being prepared by the Associated Chambers of Commerce on the lines of the instructions they had received from about 100 Chambers throughout the country. This draft Bill included this clause: "Provided that nothing in this Act shall (*a*) affect the manufacture or use of any machinery, tool, pattern, sieve, template, or other article made by measure other than metric measures." The passing of an Act on that basis would thus mean that while they would all be required to buy and sell in metric quantities, they would be at liberty to continue the use of existing weights and measures for manufacturing purposes until such time as they themselves chose to amend them.

No doubt manufacturers under the compulsion of selling their goods on the metric basis would, in course of time and at their own convenience, arrange to manufacture such goods to metric dimensions, but it was important to note that the above provision would have the effect of allowing each manufacturer to fix the length of his own transition period, and in that way unnecessary hardship would be avoided.

Engineers, for instance, knew that in the normal course of development of their industry the existing patterns at any given date became either worn out or obsolete in design within a fairly limited period. Surely it would be possible under that provision to continue those patterns in use for manufacturing purposes as long as they were commercially useful, and when it was necessary, either from development or because they were worn out, to replace them, then they could be replaced by new ones based on the Metric System. There should be no particular hardship in that.

There was, however, a bigger question—the bigger national aspect of the question to-day. Everyone knew that in order to pay off the huge war debt we were now accumulating it would be necessary for us, after the war, to export enormously increased quantities of all kinds of British manufactured goods, and it was therefore our duty to examine, and if sound to adopt, every proposal put forward which would be even likely to assist our export trade.

Now, what had happened in the past in this connection? For years past we had turned a deaf ear to the entreaties of our Consuls and our commercial representatives abroad. Whoever had been abroad knew as well as he did that for years the peoples overseas had said to England: "If you want to increase your trade with us you must reform your systems of coinage, weights, and measures, and make it easy for your potential customers to come to you." On that ground alone the Metric System had a most powerful claim upon us. Before he left that point he would like to urge that in contemplating such disturbance as the adoption of the Metric System would bring in its train, let us not regard it as something nauseous which would always be a trouble to us. When it was done we should ourselves reap the benefits and our children would be rid of the hampering influences under which we now suffer.

He would like to say a word or two in regard to the positions of America and the United Kingdom. It was frequently urged that so long as such nations as the British Empire and the United States stood aloof there was not much hope of the Metric System being universally adopted. Why had not America adopted the Metric System in the past? He submitted it was primarily because the demand for her goods was essentially a domestic demand. Until quite recently they all knew that America had relatively no export trade. But as soon as she tackled the export problem she immediately set up the agitation: "Oh, we must have the Metric System if we are going to make a bid for the South American trade and that of the other metric countries." As soon as they set out to become exporters they appreciated the benefits of the Metric System. Now, our country was essentially an exporting nation; we must export or we could not live; therefore the arguments in favour of Great Britain being the first to make the change were in his opinion overwhelming. If we made the change in our own interests America would certainly follow and we should have true uniformity.

The closing note of the author's paper says: "In conclusion, I desire to make it quite clear that my arguments in this paper are not directed against the Metric System, but rather against the propaganda for the compulsory adoption of it." He had dealt very fully with that point in the lecture to which the President had done him the honour to refer, and he would read one paragraph:—

"A favourite argument against our compulsory adoption of the Metric System is that by merely prolonging the present permissive use of the Metric System side by side with our existing British Imperial system the better system would ultimately survive. A similar argument is put forth to the effect that those who desire the introduction of the Metric System should lead the way by conducting their own business solely in that system. I submit that any such voluntary piecemeal adoption cannot be expected, as the pioneers would thereby penalise themselves by throwing themselves out of touch with their neighbours. The position is analogous to that of the Daylight Saving reform. No benefit could be derived from that reform until it was made compulsory, for had any enthusiast adopted the principle before its general adoption he would have found himself at his office or works (say) an hour before he could communicate with his clients, and when, at the end of the day his clients desired to communicate with him, they would have found that he had already gone home, having completed his day's work."

The advocates of that reform preached in vain for years the benefits of it. Either from apathy or sluggishness, even those who did not oppose it did not ask for it, and we should have gone without it altogether had it not been for the intervention of the war, which forced us to realise its many advantages, and we all now said: "Why didn't we adopt it years ago?" Why not, therefore, now throw off the shackles by which we were bound in the matter of weights and measures? The superiority of the Metric System had been demonstrated over and over again.

In conclusion, let them bear in mind the words of the Rt. Hon. A. J. Balfour, M.P., who, replying to a deputation in 1895, said: "Upon the merits of the case I think there can be no doubt whatever that the judgment of the whole civilised world, not excluding countries which still adhere to the antiquated systems under which we suffer, has long decided that the Metric System is the only rational system."

The war has quickened in them all a livelier appreciation of the defects in their national equipment and now—while public opinion was in a plastic condition—was the time to give effect to the over-due reforms which the author apparently desired to oppose.

The President requested the secretary to read the following letter from Mr. Edward Hooper:—

Would you please express to the President my regret that I find myself unable to be present to-night at the discussion of the paper by W. R. Ingalls on the Metric System, owing to an unexpected call for police duty.

It was my intention to support as far as possible the arguments so ably set out by Mr. Ingalls, although I am afraid there is but little that one can add to what has been said and written by so many writers during the past ten or twelve years against the compulsory adoption of the Metric System in Great Britain and the United States.

There is one point, however, that should perhaps be emphasised. In France, after various enactments, a Bill or "projet" was passed in July, 1837, which came into force on 1st January, 1840, whereby the possession of weights and measures other than those of the Metric System was made a penal offence; further, the use of any of the old names of units was forbidden. Yet in 1906, or nearly 70 years later, the French Minister of Commerce felt himself obliged to issue a circular to the various French Chambers of Commerce requesting them to use their influence upon merchants and their customers to induce them to abandon their use of the forbidden weights and measures.

Moreover, the Metric System was legalised in U.S.A. in May, 1866, but we do not find that it has been adopted to any great extent.

I altogether fail to see how the mining and metallurgical industries would be greatly benefitted by the compulsory adoption of the Metric System, but I do plainly recognise that manufacturers of the goods which are used by these industries would be put to an enormous expenditure, and that a large part of this expenditure would have to be borne by the industries which are represented by the institution.

POTATO DISEASE OUTBREAKS: URGENT ADVICE.

The weather generally has been favourable to the potato crops in most parts of England, but serious outbreaks of disease are reported from Barnstaple in Devon, and Devizes in Wilts. Isolated cases are also reported from Somerset, Dorset, and Cornwall. It is important that measures should be taken at once to ring-fence such outbreaks by promptly spraying crops in the surrounding districts. All crops that have not yet been sprayed should be sprayed; all crops that have been sprayed once should be sprayed again within about three weeks of the first spraying. This course is dictated alike by enlightened self interest and by patriotic feeling. The first outbreak reported this year, in Pembrokeshire, was checked by instant attention to the crops in adjoining districts. Cases in Somerset and Dorset are being dealt with on the same lines. Should a period of damp warm weather set in no doubt oubreaks will occur in other counties. There is a fairly liberal supply of horse drawn, knapsack, or hand sprayers of one kind or another in most districts, and no shortage in the supply of chemicals.

Growers who desire chemicals for spraying can obtain them at once by applying to Mr. R. Woodcock, 50, Queen Street, Exeter, who is distributing them on behalf of the Food Production Department. Applications will be immediately dealt with from any part of the country for a single case, price 24s., carriage free by goods train (enough to spray one and a third acres twice), or for any number of cases. If delivery by passenger train is required the additional cost of carriage must be forwarded when ordering; and cash must be sent with all orders. Cheques should be made out to Mr. Woodcock, not to the Department. Growers in the following counties should order their supplies of chemicals immediately from :—

Somerset: Mr. Burton, 5, Graham Road, Weston-super-Mare, Somerset; Dorset: Mr. Edgar Gordon, County Offices, Dorchester, Dorset; Wilts, Mr. Sharp, Horticultural Education Dept., County Hall, Trowbridge, Wilts; Cornwall: Mr. Borlase, County Hall, Truro, Cornwall.

The only safeguard of potatoes against "late blight" is spraying; it is not too late to spray now; the process of spraying is simple and cheap; and the grower who loses his crops or imperils the crops of his neighbours can hardly be held blameless should the magnificent promise of a bumper potato crop fail to be realised.

Sulphate of Copper Prices.—The arrangement for the sale of sulphate of copper for home consumption for agricultural purposes at the price of £50 per ton in quantities of not less than 2 cwts. f.o.r. at maker's works, will cease as from the end of July. Representations have been made that the retail price of 6½d. per lb. which was recommended in March last is now too low for small quantities. The Food Production Department does not think that 8d. per lb. is an excessive price for sulphate of copper in England and Wales.—From the Food Production Department.

National Society of Industrial Chemists.—The Provisional Executive appointed by representative chemists employed in Sheffield and district has been for some weeks considering the basis, rules, and constitutions for the proposed National Association of Industrial Chemists. Its conclusions will shortly be published in book form, and every industrial chemist and metallurgist of Great Britain and Ireland should at once apply for a membership form. About one hundred chemists have already been declared full members. Communications should be addressed to the Propaganda Committee, Bailey St. Schoolrooms, Sheffield.

PROCEEDINGS OF SOCIETIES

SOCIETY OF GLASS TECHNOLOGY.

The July meeting of the above Society was held on the 25th ult. in the School of Technology, Manchester. The chair was taken by Mr. Duncan Webb.

After the formal business was transacted a paper on "*The Action of Chemical and Physical Agents on some types of Scientific Glassware*," by J. D. Cauwood, M.Sc., S. English, M.Sc., and W. E. S. Turner, D.Sc., M.Sc., was read by the last named.

The gradual development of high-class chemical glass ware, culminating in the Jena glass of the Schott factory, was first outlined. The importance of chemical glassware in scientific development was emphasised, and it was pointed out that soon after the outbreak of war, chiefly owing to the insistent demands of the Sheffield steelworks' chemists, steps were taken to promote the manufacture of high grade chemical ware in this country. Formulæ for making the glasses were placed at the disposal of manufacturers. Prof. Jackson, of the Institute of Chemistry, Mr. F. W. Branson, of Leeds, and Dr. Travers, of London, taking a leading part in the preliminary work and in the subsequent developments. How well the glass manufacturers had risen to the occasion the results of the paper showed, and they were to be congratulated upon the fact that they had produced glasses as good if not better in some respects than the best German ones.

The method employed in the research had been to subject Jena glass, five new British resistance glasses, and a few chemical glasses made in Allied and Neutral countries to the following series of tests :—

1. Action of steam.
2. Action of boiling water.
3. Action of water under a pressure of 10 kilogrms. per sq. cm.
4. Action of water at 20° C.
5. Action of water at 80° C.
6. Action of N/10 sodium hydrate solution at 100° C.
7. Action of 2N sodium hydrate solution at 100° C.
8. Action of 2N sodium carbonate solution at 100° C.
9. Action of 5 per cent ammonium chloride solution at 100° C.
10. Action of boiling 2N ammonia solution.
11. Action of hydrochloric acid fumes.
12. Action of boiling hydrochloric acid solution.
13. Action of 2N sulphuric acid at 100° C.
14. Cracking test.

In addition each glass had been analysed. The results obtained were admirably expressed by means of lantern diagrams, and it was at once apparent that in every test applied the British glasses compared most favourably with Jena glass, in some of the tests even surpassing it.

A very representative collection of the various glasses experimented with was shown, and the effect of the various solvents on the glass surfaces thereby illustrated.

A discussion, in which Mr. C. J. Peddle, Mr. Cauwood, Mr. English, Mr. Duncan Webb, and Dr. Turner all took part, closed the proceedings.

Prior to the meeting a collection of American sands with their analyses, presented to the Society by Prof. P. G. H. Boswell, was shown, and also a collection of British sands and glasses manufactured from them. The latter collection was loaned by Messrs. Wood Bros., of Barnsley.

The next meeting of the Society will be held in Sheffield during the month of October.

NOTICES OF BOOKS.

Ozone; Its Manufacture, Properties, and Uses. By A. Vosmaer, Ph.D. London: Constable and Co., Ltd. 1916. Pp. xii + 197. Price 10s. 6d. net.

This book aims at giving the results of the author's own investigations of the nature and constitution of ozone and his experience of its manufacture, and he explains very fully his reasons for occasionally differing from the majority of other authorities. While the book does not contain very much new matter the discussions and descriptions are full and detailed, and in spite of a somewhat disjointed style it is readable and interesting. Different methods of manufacturing ozone are described, and in the case of electrical discharge methods the influence of different factors is fully discussed. The bibliography provided appears to contain the names of most of the important publications on the subject of ozone arranged chronologically.

One Hundred Points in Food Economy. By J. Grant Ramsay, F.R.E.S. London: G. Bell and Sons, Ltd. 1917. Price 1s. net.

This little book, which is provided with a preface by Prof. Halliburton, contains a good deal of useful information as to the comparative value of different kinds of foods, expressed in simple definite language in which all technical terms are avoided. Methods of economising in food are pointed out, the keynote of the text being "Knowledge is necessary for real economy." The different kinds of meat, fish, vegetables, dairy produce, &c., are considered in turn, and their suitability for various classes of people is explained, and very practical hints as to diet and digestion are included. General notes are added on food requirements in the seven stages of life, and the best kinds of foods in different circumstances are enumerated. It is to be hoped that the book will reach the readers for whom it is intended, for it cannot fail to be of considerable service to all who take counsel from it.

CORRESPONDENCE.

WAX WIRE.

To the Editor of the Chemical News.

Sir,—We want to find a maker of wax wire similar to a sample enclosed, and we shall be glad if any of your readers can give us any assistance in the matter. A lot of this material before the war formerly came from Germany, but we believe there are now makers in England, although we have not been able to find them up to now. Your assistance will be much appreciated. This material is used by iron founders, and is used in varying diameters from $\frac{1}{8}$ inch up to $\frac{1}{2}$ inch diameter.—We are, &c.,

The Northern Steel and Hardware Co, Ltd.

MISCELLANEOUS.

Society of Chemical Industry.—At the Annual General Meeting of the Society of Chemical Industry, held at Birmingham on July 18, 1917, the following resolution was submitted by the President, Dr. Charles C. Carpenter, seconded by Mr. J. H. Hoseason, and unanimously agreed to:—

> "The Council of the Society of Chemical Industry, having considered the matter, recommend, and it is hereby resolved, that—
>
> "(1) The yearly subscription for Members of the Society shall, from January 1, 1918, be 30s. in place of 25s. as at present;
>
> "(2) That the amounts payable for Life Composition under By-law 11 shall each be increased by £5; and
>
> "(3) It is therefore also resolved that By-law 10 and 11 be altered accordingly."

In terms of Paragraph 38 of the Society's Charter, a General Meeting of the Society is hereby called to be held at Broadway Chambers, Westminster, London, S.W., on Wednesday, August 15, at 4 p.m. for the purpose of confirming the above resolution.—J. P. Longstaff, General Secretary.

Announcement.—Mr. A. P. Trotter, after 21 years Government service, is returning to professional practice as a consulting engineer, and is joining Messrs. Handcock and Dykes, as partner in the firm of Handcock, Dykes, and Trotter, at 11, Victoria Street, London, S.W. 1. Mr. Trotter is B.A. of Cambridge, Member of the Institution of Civil Engineers, Member of the Institution of Mechanical Engineers, Member of Council of the Institution of Electrical Engineers, President of the Illuminating Engineering Society, Vice-Chairman of the National Illumination Committee of Great Britain (affiliated to the International Illumination Commission), Chairman of the Joint-Committee on Illuminating Engineering of the Department of Scientific and Industrial Research, and member of other scientific institutions. In 1896 he took up the post of Electrical Engineer to the Government of the Cape of Good Hope, and in 1899 he returned to London, since when he has been Electrical Adviser to the Board of Trade.

The Government and Publicity.—Two very important meetings have been convened by the Government during the last week or two, one dealing with the distribution of coal and the other with the question of the people's bread supply. Both these meetings were held exclusively for the information of the Press, and the present writer happened to be a member of the audience at both functions as the representative of one of the largest, if not the largest, series of trade newspapers owned by a single firm in the country. The avowed intention of the conveners of both meetings was to enlist the sympathy of the Press, and to secure the widest possible publicity for the Government schemes. Obviously there are no two subjects more vitally important to the people as a whole than those of bread and coal, and every employer of labour and every worker is directly affected by them. While, therefore, it is satisfactory to find that the Government is fully alive to the urgent importance of a press campaign, it is not equally satisfactory to note that the value of the trade newspapers of the country as a great publicity agent is not yet so fully realised as it should be. It is true that a start seems to have been made in this direction on a limited scale, but so far there is no indication that the Government appreciates its own opportunities of getting in touch with the classes who are most closely concerned.

The Nation's Purse.—At first sight it may seem that it is hardly the duty of those who are responsible for the conduct of trade newspapers to teach the Government Publicity Department its own business, but the fact does not seem to be appreciated that after all the workers are the people who are making the money which the nation needs, and are willing to invest it. The Coal Distribution scheme has been given a small show in a section of the trade press, and one would like to feel that this is a first step in the right direction. But there is no reason why other schemes should not be given equal publicity in the columns of newspapers that are read regularly by all classes of workers, skilled and unskilled. The Exchequer Bonds, for instance, would find scores of willing buyers if they were properly advertised in papers that are read by all the varied workers in the laundries of the country—foremen, engineers, ironers, men and women of all ages and of very various types, all making good wages and quite ready to assist the country and themselves by making small investments. The daily paper undoubtedly has its special uses as an advertising medium, but it is often glanced over and thrown away, while the trade paper is read through from end to end, consulted at intervals during the month or week before the following issue appears, and is frequently preserved for reference, and bound at the end of the year.

THE CHEMICAL NEWS

Vol. CXVI., No. 3012.

THE COMPLEXITY OF THE CHEMICAL ELEMENTS.*

By Prof. FREDERICK SODDY, M.A., F.R.S.

The elements of the chemist are now known to be complex in three different senses. In the first sense the complexity is one that concerns the general nature of matter, and therefore of all the elements in common to greater or less degree. It follows from the relations between matter and electricity which have developed gradually during the past century as the result of experiments made and theories born within the four walls of this Institution. Associated initially with the name of Davy and Faraday, they have only in these days come to full fruition as the result of the very brilliant elucidation of the real nature of electricity by your distinguished Professor of Physics, Sir Joseph Thomson. Such an advance, developing slowly and fitfully, with long intervals of apparent stagnation, needs to be reviewed from generation to generation, disentangled from the undergrowth that obscures it, and its clear conclusions driven home. This complexity of the chemical elements is a consequence of the condition that neither free electricity nor free matter can be studied alone, except in very special phenomena. Our experimental knowledge of matter in quantity is necessarily confined to the complex of matter and electricity which constitutes the material world. This applies even to the "free" elements of the chemist, which in reality are no more free then than they are in their compounds. The difference is merely that, whereas in the latter the elements are combined with other elements, in the so-called free state they are combined with electricity. I shall touch but briefly on this first aspect, as in principle it is now fairly well understood. But its consistent and detailed application to the study of chemical character is still lacking.

The second sense in which the elements, or some of them at least, are known now to be complex has, in sharp contrast to the first, developed suddenly and startlingly from the recognition in radio-active changes, of different radio-elements, non-separable by chemical means, now called isotopes. The natural corollary of this is that the chemical element represents rather a type of element, the members of the type being only chemically alike. Alike they are in most of those properties, which were studied prior to the last decade of last century and which are due, as we now think, to the outer shells of the atom, so alike that all the criteria, hitherto relied upon by the chemist as being the most infallible and searching, would declare them to be identical. The apparent identity goes even deeper into the region reached by X-ray spectrum analysis which fails to distinguish between them. The difference is found only in that innermost region of all, the nucleus of the atom, of which radio-active phenomena first made us aware.

But though these phenomena pointed the way, and easily showed to be different what the chemist and spectroscopist would have decided to be identical, it did more. It showed that although the finer and newer criteria, relied upon by the chemist in his analysis of matter, must of necessity fail in these cases, being ultimately electrical in character, yet the difference should be obvious in that most studied and distinctive characteristic of all—the criterion by which Dalton first distinguished the different kinds of atoms—the atomic weight. Those who have devoted themselves to the exact determination of these weights have now confirmed the difference in two separate cases, which, in absence of what perhaps they might regard as "preconceived notions," they were unable to discover for themselves. This is the experimental development to which I wish more especially to direct your attention. It indicates that the chemical analysis of matter is, even within its own province, superficial rather than ultimate, and that there are indefinitely more distinct elements than the ninety-two possible types of element accommodated by the present periodic system.

The third sense in which the elements are known to be complex is that which, in the form of philosophical speculations, has come down to us from the ancients, which inspired the labours of the alchemists of the Middle Ages, and which in the form of Prout's hypothesis has reappeared in scientific chemistry. It is the sense that denies to Nature the right to be complex, and from the earliest times, faith out-stripping knowledge, has underlain the belief that all the elements must be built up of the same primordial stuff. The facts of radioactive phenomena have shown that all the radio-elements are indeed made up out of lead and helium, and this has definitely removed the question from the region of pure speculation. We know that helium is certainly a material constituent of the elements in the Proutian sense, and it would be harmless, if probably fruitless, to anticipate the day of fuller knowledge by atom building and unbuilding on paper. Apart altogether from this, however, the existence of isotopes, the generalisation concerning the Periodic Law that has arisen from the study of radio-active change on the one hand and the spectra of X-rays on the other, and experiments on the scattering of α particles by matter, do give us for the first time a definite conception as to what constitutes the difference between one element and another. We can say how gold would result from lead or mercury, even though the control of the processes necessary to effect the change still eludes us. The nuclear atom proposed by Sir Ernest Rutherford, even though, admittedly, it is only a general and incomplete beginning to a complete theory of atomic structure, enormously simplifies the correlation of a large number of diverse facts. This and what survives of the old electronic theory of matter, in so far as it attempted to explain the Periodic Law, will therefore be briefly referred to in conclusion.

The Free Element a Compound of Matter and Electricity.

Although Davy and Faraday were the contemporaries of Dalton, it must be remembered that it took chemists fifty years to put the atomic theory on a definite and unassailable basis, so that neither of these investigators had the benefit of the very clear view we hold to-day. Davy was the originator of the first electro-chemical theory of chemical combination, and Faraday's dictum, "the forces of chemical affinity and electricity are one and the same," it is safe to say, inspires all the modern attempts to reduce chemical character to a science in the sense of something that can be measured quantitatively, as well as expressed qualitatively. Faraday's work on the laws of electrolysis and the discovery that followed from it, when the atomic theory came to be fully developed, that all monovalent atoms or radicles carry the same charge, that divalent atoms carry twice this charge and so on, can be regarded to-day as a simple extension of the law of multiple proportions from compounds between matter and matter to compounds between matter and electricity. Long before the electric charge had been isolated, or the properties of electricity divorced from matter discovered, the same law of multiple proportions which led, without any possibility of escape, to an atomic theory of matter, led, as Helmholtz pointed out in his well-known Faraday lecture to the Chemical Society in this Theatre in 1881, to an atomic theory of electricity.

The work of Hittorf on the migration of ions, the bold and upsetting conclusion of Arrhenius that in solution many of the compounds hitherto regarded as most stable exist dissociated into ions, the realisation that most of the reactions that take place instantaneously, and are utilised for the identification of elements in chemical analysis, are reactions of ions rather than of the element in question, made very familiar to chemists the enormous difference between the properties of the elements in the charged and in the electrically neutral state.

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* A Lecture delivered at the Royal Institution, May 18, 1917.

More slowly appreciated, and not yet perhaps sufficiently emphasised, was the unparalleled intensity of these charges in comparison with anything that electrical science can show, which can be expressed tritely by the statement that the charge on a milligrm. of hydrogen ions would raise the potential of the world 100,000 volts. Or, if we consider another aspect, and calculate how many free hydrogen ions you could force into a bottle without bursting it, provided, of course, that you could do so without discharging the ions, you would find that, were the bottle of the strongest steel, the breech of gun, for example, it would burst, by reason of the mutual repulsion of the charges, before as much was put in as would, in the form of hydrogen gas, show the spectrum of the element in a vacuum tube.

Then came the fundamental advances in our knowledge of the nature of electricity, its isolation as the electron, or atom of negative electricity, the great extension of the conception of ions to explain the conduction of electricity through gases, the theoretical reasoning, due in part to Heaviside, that the electron must possess inertia inversely proportional to the diameter of the sphere on which it is concentrated by reason of the electro-magnetic principles discovered by Faraday, leading to the all-embracing monism that all mass may be of electro-magnetic origin.

This put the coping-stone to the conclusion that the elements as we apprehend them in ordinary matter are always compounds. In the "free" state they are compounds of the element in multiple atomic proportions with the electron. The ions, which are the real chemically uncombined atoms of matter, can no more exist free in quantity than can the electrons.

The compound may be individual as between the atom and the electron, or it may be statistical, affecting the total number merely of the opposite charges, and the element presumably will be an insulator or conductor of electricity accordingly. Analogously, with compounds, the former condition applies to unionised compounds such as are met with in the domain of organic chemistry or, ionised, as in the important classes of inorganic compounds, the acids, bases, and salts. Just as the chemist has long regarded the union of hydrogen and chlorine as preceded by the decomposition of the hydrogen and chlorine molecule, so he should now further regard the union itself as a decomposition of the hydrogen atom into the positive ion and the negative electron, and a combination of the latter with the chlorine atom.

One of the barriers to the proper understanding and quantitative development of chemical character from this basis is, perhaps, the conventional idea derived from electrostatics, that opposite electric charges neutralise one another. In atomic electricity or chemistry, though the equality of the opposite charges is a necessary condition for existence, there is no such thing as neutralisation, or the electrically neutral state. Every atom being the seat of distinct opposite charges, intensely localised, the state of electric neutrality can apply only to a remote point outside it, remote in comparison with its own diameter. We are getting back to the conception of Berzelius, with some possibility of understanding it, that the atom of hydrogen, for example, may be strongly electro-positive, and that of chlorine strongly electro-negative, with regard to one another, and yet each may be electrically neutral in the molar sense. Some day it may be possible to map the electric field surrounding each of the ninety-two possible types of atom, over distances comparable with the atomic diameter. Then the study of chemical character would become a science in Kelvin's sense, of something that could be reduced to a number. But the mathematical conceptions and methods of attack used in electro statics for macroscopic distances are ill-suited for the purposes of chemistry, which will have to develop methods of its own.

We have to face an apparent paradox that the greater the affinity that binds together the material and electrical constituents of the atom, the less is its combining power in the chemical sense. In other words, the chemical affinity is in inverse ratio to the affinity of matter for electrons. The helium atoms offer a very simple and instructive case. Helium is non-valent and in the zero family, possessing absolutely no power of chemical combination that can be detected. Yet we know the atom possesses two electrons, for in radio-active change it is expelled without them as the α-particle. The discharge of electricity through it and positive-ray analysis show that the electrons, or certainly one of them, are detachable by electric agencies, although not by chemical agencies. One would expect helium to act as a diad, forming helides analogous to oxides.

Prof. Armstrong for long advocated the view that these inert gases really are endowed with such strong chemical affinities that they are compounds that have never been decomposed. They certainly have such strong affinities for electrons that the atom, the complex of the + ion and electrons, cannot be decomposed chemically. Yet, in this case, where the affinity of the matter for the electron it at a maximum, the chemical combining power is absent.

These gases seem to furnish the nearest standard we have to electric neutrality in the atomic sense. The negative charge of the electrons exactly satisfy the positive charge of the matter, and the atomic complex is chemically, because electrically, neutral. In the case of the electro-positive elements, hydrogen and the alkali-metals, one electron more than satisfies the positive charge on the ion, and so long as the equality of opposite charges is not altered, the electron tries to get away. In the case of the electro-negative elements, such as the halogens, the negative charge, though equal presumably to the positive, is not sufficient to neutralise the atom. Hence these groups show strong mutual affinity, one having more and the other less negative electricity than would make the system atomically neutral like helium. The electron explains well the merely numerical aspect of valency. But chemical combining power itself seems to require the idea that equal and opposite charges in the atomic sense are only exactly equivalent in the case of the inert gases. None of these ideas are now new, but their consistent application to the study of chemical compounds seems curiously to hang fire, as though something were still lacking.

It is so difficult for the chemist consistently to realise that chemical affinity is due to a dissociating as well as to a combining tendency and is a differential effect. There is only one affinity, probably, and it is the same as that between oppositely charged spheres. But, atomic charges being enormous and the distances over which they operate in chemical phenomena being minute, this affinity is colossal, even in comparison with chemical standards. What the chemist recognises as affinity is due to relatively slight differences between the magnitude of the universal tendency of the electron to combine with matter in the case of the different atoms. Over all, is the necessary condition that the opposite charges should be equivalent, but this being satisfied, the individual atoms display the tendencies inherent in their structure, some to lose, others to gain electrons, in order, as we believe from Sir Joseph Thomson's teaching, to accommodate the number of electrons in the outer-most ring to some definite number. Chemical affinity needs that some shall lose as well as others gain. Chemical union is always preceded by a dissociation. The tendency to combine, only, is specific to any particular atom, but the energy and driving power of combination is the universal attraction of the + for the − charge, of matter for the electron.

The Electrical Theory of Matter.

Another barrier that undoubtedly exists to the better appreciation of the modern point of view, even among those most willing to learn, is the confusion that exists between the earlier and the present attempt to explain the relation between matter and electricity. We know negative electricity apart from matter as the electron. We know positive electricity apart from the electron, the hydrogen ion and the radiant helium atom or a particle of radio-active change for example, and it *is* matter in the free or electrically uncombined condition. Indeed, if you want to find matter free and uncombined, the simple elementary particle of matter in the sense of complexity being discussed, you will go, paradoxically, to what the chemist terms a compound rather than to that which he terms the free element. If this compound is ionised completely it constitutes the nearest approach to matter in the free state. Thus all acids owe their common acidic quality to really free hydrogen, the hydrogen ion, a particle more different from the hydrogen atom than the atom is from the hydrogen molecule.

Positive electricity is thus emphatically not the mere absence of electricity, and any electrical theory of matter purporting to explain matter in terms of electricity does so by the palpable sophistry of calling two fundamentally different things by the same name. The dualism remains whether you speak of matter and electricity, or of positive and negative electricity, and the chemist would do well to stick to his conception of matter until the physicist has got a new name for positive electricity which will not confuse it with the only kind of electricity that can exist apart from matter.

On the other hand, the theory of the electro-magnetic origin of mass or inertia is a true monism. It tries to explain consistently two things—the inertia of the electron and the inertia of matter—by the same cause. The inertia of the former being accounted for by the well-known electro-magnetic principles of Faraday, by the assumption that the charge on the electron is concentrated into a sphere of appropriate radius; the 2000-fold greater inertia of the hydrogen ion, for example, can be accounted for by shrinking the sphere to one-two-thousandth of the electronic radius.

But the electrical dualism remains completely unexplained. Call the electron E and the hydrogen ion H. The facts are that two E's repel one another with the same force and according to the same law as two H's repel each other, or as an H attracts an E. These very remarkable properties of H and E are not explained by the explanation of the inertia. Are E and H made up of the same stuff or of two different stuffs? We do not know, and certainly have no good reason to assume, that matter minus its electons is made of the same thing as the electron. We have still to reckon with two different things.

(To be continued).

NOTES ON

SOME FIRECLAYS AND REFRACTORY STONE USED IN THE GLASS INDUSTRY.

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The particular type of refractory material used in the construction of a furnace for glass-making depends largely upon the conditions under which it is likely to be heated. Thus, for the crown of a furnace where the refractory material is required to withstand a high temperature, but is not subjected to the chemical action of the glass during the process of manufacture, or to the mechanical action of the slowly moving fluid, silica bricks are usually regarded as most suitable. They are quite sufficiently refractory at the temperatures usually attained in a glass furnace, and if due care be taken to allow for their expansion, particularly in the earlier stages of the life of the furnace, they provide an efficient and durable crown which has one great advantage over a crown made from fireclay bricks, in that any corners or small portions which may be shot off and fall into the metal are much more readily dissolved and incorporated in the glass.

For the sides and bottom of a tank furnace the conditions are different and the type of refractory material must be altered to suit the changed conditions. Not only must the material used be refractory in the sense that it offers a high resistance to deformation through the action of heat alone, but it must also resist chemical attack both by the batch materials and the glass, and must also possess sufficient mechanical strength to resist the abrasive action due to the "washing" effect of heavy weights of fused materials. For the construction of the sides and bottoms of tank furnaces, large blocks are used in preference to bricks. Such blocks are sometimes made from fireclay and sometimes from a particular "firestone" obtained almost exclusively from Durham. Opinions differ considerably, even amongst men with considerable practical experience of both types of blocks, as to their relative merits, but the balance of opinion appears to be that for floor blocks and side blocks below the actual level of the glass in the tank under average working conditions, stone blooks are preferable, whereas at the actual surface level, where they are subjected to the mechanical action of the fluid glass, fireclay blocks are more efficient.

Analyses and tests have been made of a South Yorkshire stone in order to ascertain its suitability for the purpose. Similar tests have also been made with samples of fireclays such as are usually used in the glass industry, both for pot-making and for tank-block making.

The materials investigated were—

A. Stone from Mexborough.
B. ,, ,, Wickersley, near Rotherham.
C. Stone from Penshaw, Durham.
D. Fireclay from Stourbridge.
E. ,, ,, Grossalmerode.
F. ,, ,, Huddersfield.
G. ,, ,, Halifax.
H. ,, ,, Church Gresley.

The results of the analyses of the first five materials are as follows :—

	A.	B.	C.	D.	E.
Silica	80·96	83·13	89·50	62·76	74·66
Alumina	10·96	8·825	6·23	22·79	14·65
Iron oxide ..	1·32	2·225	0·77	1·96	1·30
Titanium oxide..	0·80	0·70	0·65	2·12	2·50
Lime..	0·30	0·31	0·27	0·38	0·55
Magnesia.. ..	0·50	0·16	0·31	0·23	0·19
Potash	2·48	2·06	0·84	0·92	0·64
Soda	1·10	0·87	0·44	0·34	0·20
Loss on ignition	2·14	2·03	1·58	8·91	5·65

The percentage of titanium oxide in the two clays D and E was unusually high.

In the case of the three stone analyses, the loss on ignition probably gives a fair estimate of the proportion of clay present as binding material. It will be noticed that the silica content is considerably bigher in the Durham stone than in either of the Yorkshire samples.

In addition to the ordinary analysis, the three samples of stone were ground to coarse powder and subjected to treatment with sulphuric acid, followed by alternate treatment with caustic soda and hydrochloric acid, as in the "rational" analysis of clays. The clay bind was thereby removed practically completely from all three samples, leaving a clean white residue. That from the Durham stone consisted very largely of clear quartz grains and a little mica and felspar. The residue from the Yorkshire stones also consisted mainly of quartz grains which were smaller in average size than those from the Durham stone, and were accompanied by much more felspar, as indeed would be expected from the comparatively high alkali content of the stones

The contraction due to drying and firing the fireclays and stones was also investigated. For this purpose the samples of stone being cut into small slabs, and the clays brought into the plastic state by the addition of water, and when of average working consistency moulded into small tiles. The amount of water required to bring the dry clay into the plastic condition most suitable for working gives a rough comparison of the plasticity of the various clays. The three English fireclays—D, F, and G —each required about the same amount of water, namely, from 18 to 18½ per cent. The Grossalmerode clay, which contained a large quantity of finely divided silica, required rather more, namely, 19½ per cent, whilst the plastic clay from Church Gresley required as much as 24½ per cent of added water.

The tiles were very gradually air dried, and then heated at different temperatures for periods of six hours, when the following contractions took place.

Percentage Contraction on Drying and Firing.

Material.	Dried at 105°	Heated for six hours at		
		600°	1000°	1450°
A	—	—	—	—
B	—	—	+1·1 exp.	+1·5 exp.
C	—	—	+0·7 exp.	+3·5 exp.
D	6	6	7½	11
E	5½	5½	6½	10
F	6	6	7	10
G	5	5½	6	8¾
H	6½	7	11½	17

The above figures represent total contractions from the plastic state to each respective stage.

In the case of the stone slabs an expansion was observed, very slight at 1000°, but much more significant at 1450°, particularly in the case of the Durham stone. This expansion, due to the change in the silica from quartz to tridymite, must be allowed for in building a tank bottom. In works practice, the blocks are sometimes simply laid side by side, with no binding material between, and a free space, amounting to about ⅛ in. to the foot, left between them in the "green" state. On heating, the expansion of the blocks closes up the spaces and yields a compact floor.

With the Yorkshire stones, at the highest temperature the fusible portion (felspar) melted, and drew away somewhat from the quartz grains.

If used for a tank furnace sides, it is very necessary that the blocks should be set in their original bedding position, whilst for tank bottoms in a direction perpendicular to this position. In other words, the metal in the tank should be across the grain of the stone. If set otherwise, that is, with the grain parallel to the metal, spalling is liable to occur, and plates of stone break away from the surface. Corrosion occurs to the greatest extent near to the melting end of the tank, where the stones are exposed to the action of fused alkalis in the batch mixtures before these enter fully into combination with the sand. The fused glass does not appear to attack the stone blocks seriously in the "fining" section of the tank, where the heat is greatest. The corrosion is regular, and the face of the stone is eaten away evenly. "Pitting" does not occur to the same extent as with fireclay blocks.

In regard to pot furnaces, the refractory problem is somewhat different. A certain degree of plasticity is essential in the material in order to enable the pots to be built up. It is also necessary that a close-grained body should result after firing, as, if porous, the pot would be very susceptible to attack by the molten glass, and this attack is usually more pronounced in a pot than in a tank furnace, since pot furnace metal usually contains a fair proportion of lead. The heating conditions are also somewhat different, as in a pot furnace the heat necessary for the fusion and fining processes must be conducted through the material of the pot walls. Excessive thickness is therefore a drawback. To diminish the contraction of the clay during drying and firing, and to ensure that this contraction takes place evenly and regularly, the raw clay is always mixed with a certain proportion of burnt clay (or grog). This not only assists in the drying and firing of the pot, but provides a skeleton framework to support the plastic binding clay. The proportion of grog which should be added depends largely upon the plasticity of the binding clay. Generally speaking, as much grog should be added as possible without impairing the working properties of the prepared clay. The binding clay may with advantage be a mixture of a refractory, non-plastic clay with a more plastic clay to ensure a close bind between clay and grog. The grog should be burnt as completely as possible to reduce its subsequent contraction to a negligible amount. A certain proportion of very fine grog is not detrimental, since the pots, once heated up, undergo no drastic temperature changes; but the relative proportion of fine and coarse grog should be kept constant once the most favourable mixture has been ascertained. Very fine grog increases the mechanical strength of the pot, but has much less influence on the contraction of the prepared clay than an equal weight of coarser grog. Harrop (*Trans. Amer. Cer. Soc.*, 1916, xviii., 165) recommends raw clay burnt and ground specially for grog, for the reason that such grog is harder, denser, and more angular in grain than either ground potsherds or prepared clay which has been shaped into suitable blocks and then fired and ground up for use as grog.—*Journal of the Society of Glass Technology.*

STUDIES OF THE CARBONATES.*

HYDROLYSIS OF SODIUM CARBONATE AND BICARBONATE AND THE IONISATION CONSTANTS OF CARBONIC ACID.

By CLARENCE ARTHUR SEYLER
and
PERCY VIVIAN LLOYD.

(Concluded from p. 64).

Addendum.

Frary and Nietz (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2271) have recently published a series of experiments on the hydrogen concentration of solution of pure sodium carbonate. By similar experiments on sodium hydroxide (the hydrogen concentration being measured by the electrometric method), they arrived at a very improbable figure for k_w, namely, $1{\cdot}76 \times 10^{-14}$ at 25°.

Johnston (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 954) considers that this result is explained by the neglect of contact potentials, and that the most accurate figure obtainable is $0{\cdot}8 \times 10^{-14}$ (Lewis and Randall, *Ibid.*, 1914, xxxvi., 1979). This agrees with the value we have adopted. Frary and Nietz's value seems impossible, since it would lead to a figure for $\frac{k_w}{k_3} = 28 \times 10^{-5}$ with the ordinary accepted value for k_3, but nearer 40×10^{-5} with our value for k_3.

No investigator has found values approaching these figures. Frary and Nietz themselves, even at extreme dilutions (N/100), find only $19{\cdot}7 \times 10^{-5}$, in agreement with our observations on the rate of hydrolysis of ethyl acetate. Nevertheless, in considering their further results one is justified in using their value of k_w with their own experiments.

Their experimental constant represents what we call—

$$k_d = \frac{C_{NaOH} \times C_{NaHCO_3}}{C_{Na_2CO_3}}.$$

Using the ionisation constants α' for sodium hydroxide, α for sodium bicarbonate, and β for sodium carbonate (with respect to the CO_3 ion), we have—

$$\frac{k_w}{k_3} = k_d \; \frac{\alpha'\alpha}{\beta}.$$

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* *Transactions of the Chemical Society*, cxi., 1917.

TABLE D.

Concentration of sodium carbonate. Equivalents per litre × 10³.	α'.	α.	$k_d \times 10^5$.	β.	β (S. and L.) at same Na concentration.	β (S. and L.) at same Na ion concentration.
4000	0·738	0·462	3·50	0·060	—	—
3000	0·728	0·453	3·62	0·060	—	—
2000	0·758	0·490	3·90	0·073	—	—
1416	0·784	0·536	4·45	0·095	—	—
1000	0·807	0·590	4·80	0·116	0·144	0·20
400	0·849	0·711	7·00	0·214	0·271	0·33
200	0·889	0·757	9·10	0·311	0·368	0·38
100	0·916	0·797	11·10	0·411	0·464	0·50
40	0·926	0·848	14·80	0·590	—	—
20	0·931	0·877	17·60	0·729	—	—
10	0·935	0·917	19·70	[0·857]	—	—

Taking the limiting value for this at high dilutions to be $19{\cdot}7 \times 10^{-5}$, we can calculate β by the formula $\beta = \frac{k_d}{k_w/k_3}\alpha'\alpha$.

[It is not necessary that α, α', and β shonld be the value unity at infinite dilution, but only that $\beta = \alpha\alpha'$. At high dilutions, $\alpha' = \alpha$ nearly, so that $\beta = \alpha^2$ is the condition that $k_d = \frac{k_w}{k_3}$].

Frary and Nietz give the data shown in Table D, from which we calculate β. We follow them in using for α and α' the values for the estimated sodium ion concentration, but the results would not be appreciably altered by taking the values for the total sodium concentration.

It is worthy of note that the values used by Frary and Nietz for the total sodium ion concentration agree very well with those which we find. We have shown that $[\mathrm{Na}] = c(\alpha + \beta)$, where c is the concentration of the sodium carbonate in mgrm.-molecules per litre.

The degree of dissociation of the carbonate as regards sodium ions (that is, the fraction of the total sodium existing as ions) is therefore $\frac{[\mathrm{Na}]}{2c} = \frac{\alpha + \beta}{2} = \beta'$. We compare $\frac{\alpha + \beta}{2}$ with β', calculated by Frary and Nietz from the conductivity (α is here assumed to be the same as for sodium acetate at the same molecular concentration):—

$2c$.	α.	β.	$\frac{\alpha+\beta}{2}$.	β'.
1000	0·636	0·144	0·39	0·39
400	0·731	0·271	0·50	0·47
200	0·782	0·368	0·57	0·54
100	0·822	0·463	0·64	0·60

This agreement must mean that the mobility of the $\mathrm{NaCO_3}$ ion is not far removed from that of the $\mathrm{CO_3}$ ion, but, judging from the lower dilutions, is probably somewhat smaller.

The conductivity, therefore, is a fair measure of the sodium ion concentration, assuming that at infinite dilution the ions are Na and $\mathrm{CO_3}$.

The results of Frary and Nietz for β are of the same order as those obtained by us at the same total sodium concentration, although a little lower, and therefore do not vary in the direction required by comparison at the same sodium ion concentration.

Auerbach and Pick's Results (*Arb. Kais. Gesundheitsamt*, 1911, xxxviii., 243).—These authors have investigated the hydroxyl concentration of carbonates and bicarbonates and mixtures by colorimetric methods, and arrived at values for k_3 agreeing with previous investigators, namely, about 6×10^{-11}. They realised the importance of the degree of ionisation, but were hampered by the difficulty of forming an estimate of this factor. They also investigated the theory of the subject, but, as we think, neglected to introduce the degree of ionisation at the right stage. They concluded that the hydroxyl concentration of a pure bicarbonate is independent of the concentration, a result which is opposed to our experience.

For mixtures of carbonate and bicarbonate they obtained for N/10-solutions $\frac{[\mathrm{H}] \times C_{\mathrm{Na_2CO_3}}}{C_{\mathrm{NaHCO_3}}} = 7{\cdot}3 \times 10^{-11}$.

For these mixtures $k_3 = \frac{[\mathrm{H}] \times C_{\mathrm{Na_2CO_3}}}{C_{\mathrm{NaHCO_3}}} \times \frac{\beta}{\alpha}$.

Inserting our values $\beta = 0{\cdot}464$, $\alpha = 0{\cdot}783$, we get $k_3 = 4{\cdot}32 \times 10^{-11}$, in very good agreement with our estimate.

For N/5-solutions they obtained—

$$\frac{[\mathrm{H}] \times C_{\mathrm{Na_2CO_3}}}{C_{\mathrm{NaHCO_3}}} = 8{\cdot}1 \times 10^{-11}.$$

Putting $\beta = 0{\cdot}38$, $\alpha = 0{\cdot}71$, we obtain $k_3 = 4{\cdot}33 \times 10^{-11}$.

These are the most favourable results for accuracy. Pure bicarbonate solutions are difficult to prepare and keep, since slight alterations of the free carbonic acid make large differences in the hydroxyl concentration.

The authors themselves lay little stress on their colorimetric measurements for pure carbonates. For bicarbonates, however, they find a value $6{\cdot}5 \times 10^{-11}$ in N/5- as well as in N/10 solutions, and state that the hydroxyl concentration is independent of concentration.

Hydroxyl Concentration of Mixtures of Carbonates and Bicarbonates.

Auerbach and Pick, on the assumption that the salts are fully ionised, deduce the formula—

$$k_3 = [\mathrm{H}]\frac{b}{a} + [\mathrm{H}]^2\frac{a + 2b}{ak_2},$$

where a is the amount of sodium bicarbonate and b that of the carbonate (in mgrm.-molecules per litre) originally present, without regarding the hydrolysis.

For pure bicarbonates, $b = 0$, we get $k_3k_2 = \mathrm{H}^2$, so that the hydroxyl concentration appears to be independent of the concentration. This would still be the case if we introduced the values α and β into the above formula. However, this appears to be erroneous.

The values of α and β must be introduced from the beginning.

If a and b represent the amounts of bicarbonate and carbonate regarded as fully dissociated, then the hydrolysis is represented by $2\mathrm{NaHCO_3} = \mathrm{Na_2CO_3} + \mathrm{H_2CO_3}$, and the bicarbonate really present is $C_{\mathrm{NaHCO_3}} = a - 2[\mathrm{H_2CO_3}]$, and the carbonate $C_{\mathrm{Na_2CO_3}} = b + [\mathrm{H_2CO_3}]$.

If the concentration is altered, we shall have $[\mathrm{HCO_3}] = \alpha C_{\mathrm{NaHCO_3}} = \alpha(a - 2[\mathrm{H_2CO_3}])$, so that—

$$[\mathrm{H_2CO_3}] = \frac{a - C_{\mathrm{NaHCO_3}}}{2}$$

as before, though the actual value of $[\mathrm{H_2CO_3}]$ will be different.

Also $[\mathrm{CO_3}] = \beta C_{\mathrm{Na_2CO_3}} = \beta(b + [\mathrm{H_2CO_3}])$.

Putting these values for $[\mathrm{HCO_3}]$ and $[\mathrm{CO_3}]$ into the equations—

$$k_3 = \frac{[H] \times [CO_3]}{[HCO_3]} \text{ and } k_2 = \frac{[H] \times [HCO_3]}{[H_2CO_3]}$$

and eliminating $[H_2CO_3]$ we get—

$$k_3 = [H]\frac{b}{a} \cdot \frac{\beta}{\alpha} + [H]^2 \frac{(a+2b)}{ak_2} \cdot \beta.$$

For $b=0$, that is, for pure bicarbonate, this reduces to $k_2k_3 = H^2\beta$.

Hence the hydroxyl concentration, $[OH]^2 = \frac{k_w^2}{k_2k_3}\beta$, is not independent of concentration, but varies as the square root of β.

This formula ceases to hold good for very dilute solutions.

The full expression may be deduced from the following equations:—

1. $a + b = [HCO_3] + [CO_3] + (1 - \alpha)(a - 2[H_2CO_3]) + {} + (1 - \beta)(b + [H_2CO_3]) + [H_2CO_3]$,

whence $a\alpha + b\beta = [HCO_3] + [CO_3] + [H_2CO_3](2\alpha - \beta)$.

2. $[H] \cdot [HCO_3] = k_2[H_2CO_3]$ and

3. $[H] \cdot [CO_3] = k_3[HCO_3]$.

Hence—

$$[HCO_3] = \frac{a\alpha + b\beta}{1 + \frac{k}{[H]} + \frac{[H]}{k_2}(2\alpha - \beta)}.$$

4. $2[CO_3] + [HCO_3] + [NaCO_3] + [OH] = [Na] + [H]$.

5. $[Na] = \alpha(a - 2[H_2CO_3]) + 2\beta(b + [H_2CO_3]) [NaCO_3]$.

Combining (4) and (5), we have—

6. $2[CO_3] + [HCO_3] + [OH] = {} = a\alpha + 2b\beta + 2[H_2CO_3](\beta - \alpha) + [H]$.

Substituting the values of $[HCO_3]$, $[H_2CO_3]$, and $[CO_3]$ from Equations 2, 3, and 4 in 6, and simplifying, we have, finally,—

$$7.\ k_2k_3 = \frac{(2\alpha - \beta)[H]^4 + [H]^3[\beta a(a + 2b) + k_2] + {} + [H]^2[k_2b\beta - (2\alpha - \beta)k_w] - [H]k_2k_w.}{[H]a\alpha - [H]^2 + k_w}$$

For infinite dilution $\alpha = \beta = 1$, this reduces to Auerbach and Pick's equation. It holds rigorously for all dilutions.

When a and b are not so small as to be comparable with k_2 and k_w we may neglect k_2 in the expression $\beta a(a + 2b) + k_2$ and $(2\alpha - \beta)k_w$ in $k_2b\beta - (2\alpha - \beta)k_w$, and k_w in $[H]a\alpha - [H]^2 + k_w$, and *the factor* $[H]k_2k_w$.

Also we may neglect $[H]^4$ and its coefficients, and $[H]^2$ in comparison with $[H]a\alpha$.

The formula then reduces to that previously obtained:—

$$k_3 = [H]^2 \frac{(a + 2b)}{k_2 a} \cdot \beta + [H] \frac{b\beta}{a\alpha}.$$

When $[H]$ is very small (as in mixtures containing a moderate amount of carbonate) this becomes $k_3 = H\frac{b}{a} \cdot \frac{b\beta}{a\alpha}$.

When $b = 0$ (as in pure bicarbonate) it becomes $k_2k_3 = [H]^2\beta$.

By combining 6 with 2 and 3, we get—

$$H_2CO_3 = \frac{(a\alpha + 2b\beta + [H])[H]^2 - k_w[H]}{2k_2k_3 + k_2[H] - 2(\beta - \alpha)[H]^2}.$$

At infinite dilution this becomes—

$$\frac{(a + 2b + [H])[H]^2 - k_w[H]}{2k_2k_3 + k_2[H]}.$$

$a\alpha + 2b\beta$ is not the total sodium ion concentration, but that corresponding with the $[HCO_3]$ and $[CO_3]$.

If we take the first-stage ionisation of the sodium carbonate to be the same as that of the bicarbonate at the common sodium ion concentration, then we have $[NaCO_3] = (b + [H_2CO_3])(\alpha - \beta)$, whence from Equation 5 $[Na] = a\alpha + 2b\beta + (\alpha - \beta)(b - [H_2CO_3])$. The sodium ion concentration is therefore greater than $a\alpha + 2b\beta$ (compare Johnstone, *loc. cit.*).

Since the above was written, Kendall (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 1480) has determined k_2 (the first ionisation constant of carbonic acid) at different temperatures, and finds at 0° $2{\cdot}24 \times 10^{-7}$, at 18° $3{\cdot}12 \times 10^{-7}$, and at 25° $3{\cdot}5 \times 10^{-7}$. The value $3{\cdot}5 \times 10^{-7}$ should therefore be used in conjunction with the experiments carried out at 25°.

This does not alter the ratio $\frac{k_2}{k_3}$ found by us at 25°, namely, 7120, nor does it alter the calculation of the degree of ionisation of sodium carbonate. It does, however, alter the value of k_3 (the second ionisation constant of carbonic acid), and gives a figure of $4{\cdot}91 \times 10^{-11}$ instead of $4{\cdot}27 \times 10^{-11}$. It would also give $\frac{k_w}{k_3} = 16{\cdot}7 \times 10^{-5}$ instead of $19{\cdot}2 \times 10^{-5}$ if the value of k_w is taken at $0{\cdot}82 \times {}^{-14}$ at 25°. Further careful experiments are required to determine the variation of $\frac{k_2}{k_3}$ with temperature, which would enable us to ascertain how k_3 varies with this factor.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

By IRVING LANGMUIR.

(Continued from p. 56).

Forces between Atoms in Crystals.—From our knowledge of the structure of crystals and from such properties as specific heat, compressibility, thermal coefficient of expansion, elasticity in different directions, melting point, vapour pressure, and latent heat of evaporation, it should be possible to determine the laws governing the forces around the atoms. Such a study would give us the clearest kind of insight into the nature of chemical affinity.

In view of the marked influence of temperature on the properties of liquids and solids, it is evident that the motions of the atoms in solids are of great importance. A study of specific heats gives us considerable information regarding the kinetic energy of the atoms. According to the Principle of the Equipartition of Energy, the average kinetic energy of any particle is $\frac{1}{2}kT$ for each degree of freedom, where k is the Boltzmann gas constant and is equal to $1{\cdot}372 \times 10^{-16}$ ergs per degree. (For a short description of this principle and its present significance, see Dushman, *General Electric Review*, Sept., 1914). In other words, each particle should contribute the amount $\frac{1}{2}k$ to the specific heat for each degree of freedom which it possesses. Thus for a grm.-molecule of particles ($6{\cdot}06 \times 10^{23}$) we find a specific heat of $\frac{1}{2}$ R for each degree of freedom. Here R is the gas constant ($6{\cdot}06 \times 10^{23} \times 1{\cdot}372 \times 10^{-16} = 83{\cdot}1 \times 10^6$ ergs/deg.). Expressed in calories, this gives 0·993 cal. per deg. per grm.-atom for each degree of freedom. We thus have the simple rule that the atomic or molecular heat should be numerically equal to 0·993 times the number of degrees of freedom (n) of the atoms or molecules.

Each atom of a monatomic gas has three (translational) degrees of freedom, and we should thus expect the atomic heat to be $C_v = 3 \times 0{\cdot}9935 = 2{\cdot}98$. Actually for all the monatomic gases we find exactly this value with the single exception of helium, which gives a slightly lower value.

The specific heats of most diatomic gases is approximately $C_v = 5$, from which we may conclude that there are five deg. of freedom (three translational and two rotational). The possible motion of the two atoms along the line joining them evidently does not represent a degree of freedom. However, the diatomic gases like chlorine, bromine, and iodine, which are easily dissociated into atoms, have specific heats considerably greater than 5.

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* From the *Journal of the American Chemical Society*, xxxviii No. 11.

There is thus evidence that with very strong chemical forces between atoms the number of degrees of freedom is less than with weaker forces.

The atoms of copper, silver, gold, and lead are arranged according to a simple face-centered lattice with single atoms at each point of the lattice. It is evident that there are no group molecules. Each atom must possess (at high temperatures) three deg. of freedom corresponding to the directions in which it may move.

We know, however, in accordance with Dulong and Petit's law, that the atomic heat of these metals is approximately 6·0 (see Note), and this is usually explained by assuming that the atoms vibrate in such a way that their energy is equally divided between kinetic and potential energy. When a body such as a pendulum describes *harmonic* vibrations, the time average of its kinetic energy is equal to the time average of its potential energy, if we assume that its potential energy is zero when it passes through its equilibrium position. The equipartition principle is concerned directly only with kinetic energy, but if the average potential energy is equal to the average kinetic energy, it is evident that it will contribute as much as the latter to the specific heat. Thus if the atoms of the solid body describe harmonic oscillations about their equilibrium positions, the atomic heat should be double that corresponding to the three degrees of freedom; in other words, it should be $6 \times 0{\cdot}9935 = 5{\cdot}96$.

(NOTE.—According to Dulong and Petit's Law, the atomic heats of the elements at *constant pressure* are about 6·3. The specific heat of $6 \times 0{\cdot}993$ calculated by the equipartition principle is the atomic heat at constant volume. Lewis, Nernst, Lindemann and others have shown that the atomic heats of metals at *constant volume* gradually approach the above value assymptotically at higher temperatures, but at lower temperatures the atomic heat is considerably less. Elements with atomic weight less than about 20 form an exception to this rule in that their atomic heats are less than $6 \times 0{\cdot}993$ even at room temperature).

It is often said that in this case there are three kinetic and three potential degrees of freedom. This statement is open to serious objection, for it implies that the equipartition principle is applicable to potential energy. As a matter of fact, if the forces around the atoms are such as to lead to oscillations that are not harmonic in character, there will in general be no equality between the time averages of the kinetic and potential energies. For example, let us consider a ball rolling on a surface, such as that represented in Fig. 1 (*prox.*). If the ball is displaced from its lowest position and released, it will oscillate about this position. If the displacements are small, the motion will be approximately harmonic in character. But with oscillations so large that the ball frequently mounts up on to the comparatively level parts of the surface, it is evident that the oscillations will be far from harmonic. In this case, the motion of the ball on the flatter parts of the surface will be so slow that the length of time it remains in these positions will be much larger than it would be if the slope of the surface increased steadily from the centre outwards. Thus, with such a surface the time average of the potential energy may be much greater than the time average of the kinetic energy.

The same considerations apply to the oscillations of atoms. If the restoring force acting on an atom is proportional to the displacement from the equilibrium position (condition for harmonic motion) then the average kinetic and potential energies will be equal and the atomic heat will be $6 \times 0{\cdot}993$. But if the restoring force increases more slowly than proportional to the distance (as in the case cited above), then the potential energy will be greater than kinetic energy, so that by the equipartition principle the atomic heat will be greater than $6 \times 0{\cdot}993$. On the other hand, if the restoring force increases more rapidly than the displacement, then the atomic heat will be less than $6 \times 0{\cdot}993$.

The remarkable closeness with which the atomic heats at constant volume approach the value $6 \times 0{\cdot}993$ at the higher temperatures may be taken as proof that the forces to which the atoms in solids are subjected vary approximately in proportion to the displacement of the atoms from equilibrium positions. There must then be both attractive and repulsive forces acting between the atoms. On the average, these opposing forces must just balance each other. As one atom approaches another the repulsive force must *gradually* increase and the attractive force decrease until the repulsive force greatly predominates. We cannot consider that the repulsive forces in solids are exerted only during collisions between atoms, for under these conditions there would be no potential energy, and the atomic heat would be $3 \times 0{\cdot}993$.

No adequate explanation has been offered of the repulsive forces between atoms. If matter is built up of positive and negative electricity, the ordinary electromagnetic theory would indicate that the two opposite charges would neutralise each other. Actually, however, this neutralisation only occurs to the extent of destroying the electric field at a comparatively large distance from the electrons. The positive and negative electrons are never able to destroy one another. Some cause, at present unknown, must operate to keep the positive and negative charges from approaching with less than a certain distance. It is evident that the laws governing the forces and motions of electric charges separated by distances comparable with the dimensions of atoms are in some respects radically different from the laws with which we are familiar. G. N. Lewis (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 773) believes that such considerations lead "irresistibly to the conclusion that Coulomb's law of inverse squares must fail at small distances," and that it may be necessary to modify the law "even to the extent of changing the sign of the force." This difficulty is undoubtedly connected in some way with those which have forced us to the quantum theory. Some more or less successful attempts have been made to apply this quantum theory to the structure of atoms and molecules. Bohr's theory of the hydrogen atom has been remarkably successful in that it enables one to calculate all the lines in the Balmer series of the hydrogen spectrum, but his theory of the hydrogen molecule is apparently not complete, for it leads to a value of 63,000 calories for the heat of formation of H_2 from atoms, while direct measurement (Langmuir, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 417) gives 84,000 calories.

A very suggestive theory has been worked out by A. L. Parson ("A Magneton Theory of the Structure of the Atom," *Smithsonian Publication* 2371, 1915, Washington) in which he assumes that the electron itself is not merely an electric charge, but is also a magnet. Crehore (*Phil. Mag.*, 1915, xxix., 310) has developed a theory in which the magnetic field produced by the rotation of electrons in extremely small orbits (10^{-12} cm.) is assumed to play an essential part in the structure of molecules. By means of the magnetic fields, it is possible to account for both attractive and repulsive forces. Both of these theories assume that the positive electricity of the atom is distributed uniformly throughout a sphere of definite size, inside of which the electrons are located (Thomson's theory). Rutherford's work on the scattering of alpha particles, Moseley's work on X-ray spectra, and considerations based on the disintegration of the radioactive elements, all seem to compel us, however, to adopt Rutherford's theory of the atom in which the positive electricity is concentrated in the centre of the atom and the electrons revolve in one or more orbits of diameters of the order of magnitude of 10^{-8} cm. The strength of this evidence in favour of Rutherford's theory is such that it seems to the writer impossible to accept either Parson's or Crehore's theory in their present forms.

These questions will probably be satisfactorily answered only when we understand the mechanism underlying the quantum theory and know the true relationship between positive and negative electricity. We must have an explanation of the remarkable fact that the charge on an electron is *exactly* equivalent (although opposite in sign) to the unit of positive electricity (for example, the nucleus of the hydrogen atom).

At present, therefore, in an analysis of the forces between atoms, we must recognise both attractive and repulsive forces, although we cannot satisfactorily explain the mechanism of the repulsive forces. Thus, by admitting the existence of forces which prevent electrons from approaching too closely to positive charges we may accept Stark's and J. J. Thomson's theories of the general character of the forces between atoms.

There are many other properties of solids which indicate that repulsive as well as attractive forces exist between atoms, and that the repulsive forces act over distances comparable with the dimensions of atoms and not merely during collisions between atoms.

The compressibility and coefficient of thermal expansion are two such properties. In the case of ideal gases, these quantities vary with the pressure and temperature in a way that indicates that the volume would be zero if the atoms or molecules were brought into contact.

From the smallness of the coefficient of expansion of solids we must conclude that even at the absolute zero of temperature, the volume of crystals would not be so very much less than at room temperature. Furthermore, there are no indications that the compressibility would become zero even at the absolute zero. These facts are further evidence that the atoms of solids tend to be held in definite equilibrium positions by forces which vary approximately proportionally to the displacements of the atoms from these positions.

Nernst, Einstein, and Lindemann have shown that the natural frequency of vibration of the atoms of elements may be calculated by three independent methods, based respectively on measurements of the specific heat at low temperatures, the compressibility, and the melting point. The fairly good agreement between these methods lends further support to the belief that the atoms vibrate about equilibrium positions.

The intensity of the higher orders in the X ray spectrum of crystals increases as the temperature of the crystal is lowered. This effect, known as the Debye effect, constitutes striking proof of the heat vibrations of the atoms, and should lead to quantitative measurements of these vibrations.

The magnitude of the heat conductivity of solids, especially metals, throws some interesting light on the character of atomic vibrations. Let us imagine all the atoms in the surface layer of a solid to have their temperature suddenly raised by a given amount. This layer will then rapidly cool and will approach the temperature of the underlying layers. The rapidity with which this temperature equalisation takes place will measure the rate at which a motion of one atom affects the adjacent ones. A simple approximate calculation (see Langmuir, *Phys. Rev.*, 1916, viii., 149) gives for the time necessary for the temperature increment of the surface layer to fall to 37 per cent of its initial value:—

$$t_r = \frac{3k}{h\sigma} \qquad (1)$$

Here k is the Boltzmann gas constant $1{\cdot}372 \times 10^{-16}$, h is the heat conductivity of the solid, and σ is the distance between adjacent atoms. The quantity t_r is exactly analogous to Maxwell's "time of relaxation" in a gas which is the time needed for any abnormal distribution of kinetic energy among gas molecules to subside to $1/e^{th}$ of its original value.

For copper we thus find $t_r = 4{\cdot}6 \times 10^{-16}$ seconds. This has been calculated on the assumption that each atom can receive heat from one direction only. When we consider that a single atom in the interior may receive energy from six different directions, it seems probable that the real time of relaxation of a single copper atom is about 10^{-16} seconds. Now the atomic frequency calculated from the compressibility by Einstein's method is $5{\cdot}6 \times 10^{12}$, or the time necessary for an atom to complete a single oscillation, the reciprocal of this or $1{\cdot}8 \times 10^{-13}$ seconds. Thus the time required for an atom nearly to reach equilibrium with its neighbours is only 1/1800th of the time of a single oscillation. (A. H. Compton, *Phys. Rev.*, 1916, vii., 341, in a "Physical Study of the Thermal Conductivity of Solids," reached the conclusion "that the average distance through which the energy of an atomic collision in a crystal is transmitted is approximately inversely proportional to the temperature *and is many times the distance between atoms*." In many ways this is equivalent to our conclusion that the time of relaxation is small compared to the natural period of oscillation. From what has been said above, Compton's statement is open to serious objection, since we cannot look upon the repulsive forces in solids as being due to *collisions*).

Even for non-metallic substances, such as sodium chloride, the time of relaxation is always very small compared to the natural period of the atoms. This indicates that motions of a single atom must always be very highly damped. In other words, the atoms behave towards each other as though they were almost completely inelastic. However, if all the atoms are stimulated simultaneously by a periodic disturbance having a frequency corresponding to the natural frequency of the atoms, then the oscillations will be practically undamped, for there are then no adjacent atoms to which the oscillating ones can give up their energy.

We shall see that this apparent inelasticity of the atoms of solids is of great importance in the theory of evaporation, adsorption, and surface tension.

The principle of the Equipartition of Energy has been found to apply at higher temperatures to the specific heats of monatomic gases, most diatomic gases, and most elementary solids. But at low temperatures the specific heats always fall below that calculated by this principle. According to Einstein's theory, this is due to the inability of oscillators to take up energy in quantities less than $h\nu$, where h is Planck's quantum $6{\cdot}58 \times 10^{-27}$ erg deg. Whether this is the correct explanation or not, it is a fact that degrees of freedom tend to disappear at lower temperatures. Eucken has shown that at temperatures as low as 58° absolute, hydrogen molecules have only three degrees of freedom, whereas they have five at ordinary temperatures. Similarly the specific heat of helium at the lowest temperatures falls even below 2·98. Evidently, therefore, it is possible that a single atom may have less than three degrees of freedom, although it is hard for us to conceive of such a possibility.

The smaller the atomic weight of an element, and the greater the strength of the union between the atoms, the higher is the temperature at which the atomic heat begins to be normal (5·96). Thus there seems to be a relation between the natural frequency of the atoms and the deviations from the equipartition principle.

However, Trautz (*Verh. deut. physik. Ges.*, 1913, xv., 969) attempts to explain the decrease in the specific heat of hydrogen at low temperatures by assuming that for each temperature a certain fraction of the hydrogen molecules are transferred into another modification of hydrogen which has the properties of a monoatomic gas. A. H. Compton (*Phys. Rev.*, 1915, vi., 377) makes a somewhat similar assumption regarding solids, namely, that at low temperatures the atoms are agglomerated into larger aggregates in which the individual atoms lose one or more of their degree of freedom.

The specific heat of solids at ordinary temperatures is a distinctly additive property (Kopp's rule), a fact which is in itself an indication that solids are not built up of molecules. With compounds of the heavier elements, each atom contributes an equal amount (about 6·3 calories per grm.-atom at constant pressure) to the specific heat. In the case of the lighter elements, such as those forming organic compounds, the additive relations still hold fairly well, but the atomic heats of these elements must be taken to be less than 6·4. According to Kopp's rule (Nernst, *Theoretische Chemie*, 1903, 180), the following atomic heats should be taken: C = 1·8, H = 2·3, B = 2·7, Be = 3·7, Si = 3·8, O = 4·0, P = 5·4, S = 5·4, and all elements of higher atomic weighs, about 6·4.

Accurate determinations of the specific heats of organic compounds in the solid, liquid, and gaseous condition and at various temperatures will undoubtedly be of great service in establishing the character of the vibrations of the atoms, and the nature of the forces controlling them. The available data at present are very meagre and unreliable.

(To be continued).

COTTON.

By W. H. SCHERFFIUS, M.S.,
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Introduction.

In an endeavour to introduce cotton culture into this country, I should not like to create an impression that we are dealing with a comparatively new crop. Cotton culture and the use of cotton fibre is almost as old as the human family. Cotton lint was used in the manufacture of clothing during ancient times; history records the use of it eight hundred years before Christ. The ancient historian Herodotus wrote of cotton trees growing wild in India, and stated, "the fruit of which is a wool exceeding in beauty and goodness that of sheep. The Indians make their clothes of this wool." The same writer, in speaking of the clothing of Xerxes' army, mentions cotton-wool. Pliny wrote about the cotton plant in India, describing the leaves as similar to those of the mulberry, and said the inhabitants sowed the seed in the fields, and gathered crops, from which they made linen clothes. From these ancient times down to the present cotton has been grown, at some period, in almost every country in the world where tropical or subtropical conditions prevail.

During the last half-century the production of cotton has advanced with tremendous rapidity. The United States of America is far in the lead, producing approximately two-thirds of the world's crop. The Continent of Europe leads in the consumption, with Great Britain a close second, the United States third, and India fourth.

Sixty years ago less than 2,000,000 bales of 500 lbs. each of lint were produced; now something like 20,000,000 bales of 500 lbs. each are produced annually. When we consider the millions of people who are to-day either naked or only partially clothed, we realise the enormous possibilities still awaiting this industry.

In the foregoing statement no mention has been made of the scores of other uses to which cotton lint and the seed are applied, such as the manufacture of high explosives, upholstering, mattress-making, the manufacture of various food products, stock foods, and fertilisers.

With these introductory remarks it is my intention to discuss the cotton industry in so far as its possibilities and prospects affect South Africa.

Progress of the Cotton Industry.—For the past three years the Union of South Africa has produced annually approximately one half million pounds of seed cotton; of this amount there were about 170,000 lbs. of lint and 330,000 lbs. of seed. The lint has been sold at prices ranging from 6d. to 8d. per lb. There has been a demand for seed only for re-seeding purposes until recently. A Pretoria firm has been crushing the seed and selling seed meal; this new enterprise is making some headway.

Soil Suited to Cotton.—Where climatic conditions are favourable for cotton growing—that is to say, where low and middle veld conditions prevail, and with a fair rainfall —cotton can be produced on a variety of soils, such as sandy loam, black turf, alluvial, clay-loam, and calcareous soils. South Africa has large stretches of country where both soil and climatic conditions are favourable to the production of this crop. The most progress has so far been made in the middle or bush-veld of the Rustenburg district.

Cotton as compared with Mealies as a Drought Resister.—It has been proved repeatedly that cotton is far superior to mealies as a drought resister. We have a number of instances on record where farmers planted a portion of their lands to mealies and a portion to cotton; the drought was so severe that the mealies came to nothing, while the cotton gave a fair yield of lint. Last May I had a report from a farmer in the Waterburg district, who informed me that last season he planted 400 acres of mealies, and on account of the severe drought he reaped nothing. He had two acres planted to cotton, and he reaped one and a half tons of cotton. This farmer intends to plant 200 acres to cotton next season. I have had many similar cases reported. These results obtained by farmers verify results obtained at our experiment stations.

I should like to make it clear, however, that the first few weeks after the seed are sown is a very critical period. The young plants must have a moist soil until they are well established, after which they will stand a lot of drought, and still recover to a considerable extent when the rains set in again.

Profits in Cotton Culture compared to those in Mealie Culture.—The average yield of mealies per acre in South Africa is about 4 bags; placing the value at 10s. per bag will give a total profit of £2 per acre, or a net profit of about £1 per acre. A cotton crop of only 600 lbs. of seed cotton would give 200 lbs. of lint; placing an average value of 6d. per lb. on it will give a gross profit of £5 per acre, and a net profit of approximately £2 10s., and there are still 400 lbs. of seed left, which, if ground, make an excellent stock food. If a larger yield of mealies or cotton is obtained, the relative values will increase in about the same proportions as those given above.

Varieties Suited to South Africa.—In the middle or bush-veld some of the American varieties, such as Cleveland, Bancroft, Pullnot, Russell's, and Bohemian, give the best results. In the low veld, where the soil is very fertile, and on portions of the coastal belt, such as Natal and Zululand, Cook's Long Staple, Nyassaland, Allen's, and Sunflower have given the best returns. A new variety, Taylor's Long Silk Staple, is being bred at the Rustenburg Station; this variety has a beautiful long, silky staple, a scant foliage, and upright trees, which are all points in its favour, and whether it is going to be superior to some of the old-established varieties we are not yet ready to state.

All of the above varieties are annuals, and should be resown every season. I have heard of a few instances where farmers have ratooned (pruned or cut back) their cotton trees and left them over for the second season with good results, judging from their reports. When this is done the second crop of cotton usually yields a shorter and inferior lint. A perennial variety by the name of Caravonica has been tried in many parts of the Union, but the results have been very disappointing, especially in the interior. Our records show that a few farmers have been successful with it, particularly in humid coastal areas. Mr. Lofiler, of Zululand, is reported to have obtained good results with this variety.

Does Cotton Impoverish the Soil?—In theory, cotton could be grown continuously on the same soil, provided the stalks and seed are returned to the soil, as the lint is almost a pure hydrocarbon. In practice, we usually burn the stalks to prevent insects from harbouring in them during the winter, and the seeds seldom find their way back to the same land; therefore a rotation of crops is advisable, as it keeps the soil in a better physical and chemical condition. Cotton is the least exhaustive of soil fertility of most commercial crops grown in South Africa; for example, cotton requires in fertilising elements approximately two-thirds as much as wheat, one-third as much as tobacco, and a quarter as much as mealies.

In a series of fertiliser and rotation experiments we found that phosphates gave better results than either nitrogen or potash, but a complete fertiliser gave far better results than those obtained from the application of any one of the three elements. Similar results were obtained from tobacco, mealies, forage, and legumes, which indicated that the soils were deficient in phosphates.

Ginning and Seed Crushing Plants.—Ginning facilities have been greatly improved during the last two or three years. There are two ginning plants operating in Rustenburg that are capable of ginning ten times the amount of the total production of the Union; in addition, there are several smaller plants operating in different parts of the country.

When the industry has made further progress there will, no doubt, be a seed-crushing plant established to work up the seed into by-products. At the present moment certain firms have the question under consideration. Such a mill will be a great assistance to the cotton industry, as it will establish a further source of revenue.

Last year there were approximately 400,000 gallons of cotton-seed oil, valued at £48,000, sold in South Africa. Half of this quantity was sold as salad oil and half as crude manufacturing oil. At present but little cotton-seed cake is fed to stock in this country, but once it is produced here there should be no difficulty in disposing of it to dairymen and feeders of beef cattle, as it is recognised as one of the best-concentrated feeds obtainable.

Market for South African Cotton.—There is a spinning-mill at Woodstock, C.P., which is now operating 1500 spindles; this mill is kept going 24 hours daily, and they require approximately the whole output of the Union, *i.e.*, 150,000 lbs. of lint annually.

As this industry grows, their requirements of raw material will likewise increase. Further, the English and European manufacturers, who are operating more than 100,000,000 spindles, have difficulty, at times, in obtaining all the raw material they require for their mills; so far as we are concerned this demand is inexhaustible.

Prospects.—During the last two or three years the cotton industry has steadily improved, and I think I am justified in saying that there is probably no industry in South Africa at present with brigher prospects, and certainly none with greater possibilities. Once normal conditions are restored, I expect to see this industry make steady progress until cotton becomes one of the big agricultural products of the country.

In conclusion, I wish to state that seven years ago, when I took over the cotton work for the Government, the industry had been for a number of years practically discarded as hopeless, on account of the apparently insurmountable difficulties that had to be faced. Great credit is due to men like Mr. Burtt-Davy, of the Transvaal, the late General Sir Edward Brabant, of the Cape Colony, and Mr. Kirkman, of Natal, for keeping a bit of interest alive as to the possibilities of this crop during this depressed period. — *South African Journal of Science*, December, 1916.

ONE HUNDRED AND TWENTY-FIVE GERMAN DYE PATENTS.

(*From a Correspondent*).

Application for 125 licences to use German coal-tar dye patents have now been made to the Patents Court.

The last was heard on Thursday before the Court rose for the vacation, when the Morton Sundour Fabrics, Ltd., of Carlisle, asked to be allowed to manufacture under 29 patents belonging to the Badische Anilin und Soda Fabrik, Leopold Casella and Co., the Aktiengesellschaft für Anilin Fabrikation, Meister, Lucius, and Bruning, and the Chemische Fabrik Greisheim-Elektron.

The Morton Sundour Fabrics, Ltd., have already applied for licence to use eighteen patents of the same class—the anthracene series—and Mr. James Morton, its managing director, explained that they had now practically swept the German field of the dyes which had any attraction for their own particular interests. British Dyes, Ltd., of Huddersfield, have applied for between 50 and 60 German dye patents, and Messrs. L. B. Holliday and Co., of Huddersfield, for 19. A considerable proportion of the patents for which the Carlisle firm applied were post-war patents, belonging to the years 1914 and 1915, so that they gave the most modern range of fast vat-dye colours. Morton Sundour Fabrics, Ltd., have decided to separate their dye factory from the rest of their undertaking, and a separate company, the Solway Dye Co., of Murrell Hill Works, Carlisle, has been promoted by them in the last two or three weeks, to take over the manufacture of dyes on a large scale. They will produce the dyes covered by this new range of patents. The Morton Sundour Fabrics were the first in this country to make the blues, yellows, and browns of the indanthrene series and alizarine sapphirole.

Mr. A. H. Davies, M.Sc., the applicant's chief chemist, gave evidence, and the Controller of Patents, Mr. Temple Franks, intimated that he thought the licences ought to be granted.

PROGRESS OF THE WORLD'S CROPS.

The hot weather and the rains which prevailed during June throughout western and southern Europe have been favourable for all crops, improving the outlook for the greater portion. In France, in Great Britain, in Ireland, and in Italy a very notable advance is reported as to the winter-sown crops, which had suffered from the rigour of the season so generally; so that though a yield above the average is out of the question the present forecast is much more propitious than could have been expected from the recent state of these crops.

The spring-sown crops, generally speaking rather later than usual, have made up for lost time as a consequence of last month's weather, and their condition is almost everywhere an entirely satisfactory one. In Canada and in the United States the winter crops are in fair condition, having steadily recovered from the severe weather, especially in the United States. In these two countries the spring sowings are also in satisfactory condition.

In northern and central Europe, on the contrary, there is still room for complaint as regards the growing crops.

In Denmark the present situation points to a crop decidedly below average, and gives cause for some anxiety.

In Sweden the crops have made but little growth owing to the cold winter, the lateness of the spring, and the serious drought which has lasted so long in that country.

In Switzerland, on the other hand, the winter crops are well advanced in spite of drought, and an average yield is expected. The spring crops have felt the effects of the dry weather more decidedly. The same conditions prevail in European Russia, where an important improvement in the crops is reported to be principally due to recent rainfall.

From information furnished by the Governments to the International Institute of Agriculture of Rome and published in its July number of the *Bulletin of Agricultural and Commercial Statistics*, just issued, we find that the condition of the crop of wheat on July 1, 1917, was good in Spain, average in Ireland, Italy, Switzerland, Canada, and the United States, while it was mediocre in Denmark, Great Britain, and Sweden.

Rye is doing well in Spain and Ireland; it is in average condition in Italy, Switzerland, Canada, and the United States, and mediocre in Denmark and Sweden.

The barley crop is good in Spain, Scotland, and Ireland, average in England, Italy, Switzerland, Canada, and the United States, and mediocre in Denmark and Sweden. As regards oats, the outlook is good in Spain and the United States, average in Scotland, Ireland, Italy, Switzerland, and Canada. It is mediocre in Denmark, England, and Sweden.

Maize looks well in Spain, Italy, and Switzerland, and is in average condition in the United States.

The Institute's *Bulletin* for June furnished much information on the areas sown and on the forecasts of yield.

The Institute has received new data since then with regard to these matters, and such data have been inserted in the July number. We append the more important figures.

	Yield (thousands of quintals).			Percentages in 1917 compared with —	
	1917.	1916.	average 1911 to 1915.	1916 (1916=100)	the average (average =100).
Wheat—					
Spain	38,376	41,458	34,078	92·6	112 6
United States (winter) ..	109,408	131,111	146,649	83·4	74·6
Barley—					
Spain	16,655	18,912	16,138	88·1	103·2
Cotton—					
British India .	7,753	6,782	7,814	114·3	99·2

With this month is inaugurated the publication of a new supplement of the *Bulletin*, entitled "Documentary Leaflets." This supplement is specially reserved for information on products and on questions connected with agriculture which hitherto have not been included in the usual compass of the Bureau of Statistics.—*International Institute of Agriculture*, Rome, July, 1917.

JOURNAL OF THE SOCIETY OF LEATHER TRADES' CHEMISTS.

(Editorial).

Although most of us will agree that the foundation of a new Society of Leather Trades' Chemists, and of a new journal, has been rendered inevitable and necessary by the German action which has brought into being the present world war, yet to us who took prominent part in founding and carrying on the old International Association, hope for the future is not untinged with regret at the apparent failure of our efforts to bring about mutual helpfulness and good understanding between nations. The end is not yet, and possibly our work may have results in the future which we do not anticipate, for no honest work is utterly wasted; but for the present we can only devote our energies to saving what we may from the international wreck, and preventing the destruction of the fair edifice of leather chemistry which has been reared. As it is manifestly impossible for the present, and possibly for the future, to work with Germany, we must create a league of allies which will carry on, leaving Germany unfettered to find her own salvation as she best may. Hence the new society and the new journal, which will endeavour to carry on all the best traditions of the old. To do this will demand the united effort of all—not merely the professional chemists, but the tanners must aid, with money if need be—but what is still more important with sympathy and encouragement. That this aid will be freely given is not to be doubted, and both the sympathetic tone of the Leather Press, and the increased appreciation of the possibilities of chemistry by individual leather manufacturers are reassuring. Let us as chemists do what we can to justify their hopes and to realise their wishes. Much of our work during the last twenty-five years has been to increase our knowledge of first principles, and to improve the methods of analysis which are our tools, and we must not complain if this work has been only partially understood by those whose principal concern was for the harvest. There is still much to be done before we can say that our knowledge is complete, but at least we are justified in hoping for the fruits of what we have already gained, in the form not only of better control for the old, but in the suggestion of new methods of manufacture.

The man who works in the discovery of principles is essential to progress, as the sower is essential to harvest, but it is not always he who is most successful in the application of his discoveries to industrial success, and the man of practical application is not less essential to progress than the discoverer, and frequently reaps most both of the praise and of the profits. We shall endeavour to give him a prominent place in our new journal, if his native modesty will allow him to occupy it, and to risk the criticism which such prominence will no doubt entail!

Not less important than new methods is a clear and reasoned understanding of the old ones, supported by facts and accurate observation which can only be gained in practice. There has been too much tendency in the past to regard such small gains of knowledge as important trade secrets, forgetting that their full value is only obtained by comparison with the similar work of others, and that each piece may be the one thing needed to complete a general knowledge. The tendency of the day is towards syndication and co-operation, and rivalry is less between individuals than between nations.

This editorial must not be concluded without a warm acknowledgment of the debt which the Society owes to the late editor of the London Collegium, Mr. M. C. Lamb, who in a time of great difficulty boldly accepted the position, and rendered possible the immediate commencement of an allied journal. The numbers of the London Collegium will be a permanent monument to his industry under great stress of other work, and without the assistance of any adequate staff of scientific helpers on the spot to lighten his labours.

NOTICES OF BOOKS.

Food Gardening for Beginners and Experts. By H. Valentine Davis, B.Sc. London: G. Bell and Sons, Ltd. Pp. vii+44. Price 6d. net.

Detailed directions are given in this booklet to enable the amateur gardener to obtain all the year round profitable crops of hardy and easily cultivated vegetables such as are specially suitable for new soil. A plan of campaign is outlined, and methods of preparing the ground and manuring it are carefully explained. Comparatively little attention is paid to artificial manures, information as to their nature and use being regarded as outside the scope of the book. After general hints and directions each vegetable is considered in turn, and the choice of variety is discussed and dates of sowing and harvesting, &c., are stated, so that there seems to be little possibility of even the complete novice going wrong. The great importance of increasing the nation's food supply is at last being recognised, and such books as this, in which practical advice based on scientific knowledge is given in very simple language, are sure of the welcome they deserve.

Reports of the Progress of Applied Chemistry. Issued by the Society of Chemical Industry, Broadway Chambers, Westminster. Vol. I. 1916. Pp. 335. Price 3s. to Members, 5s. 6d. to others, post free.

This volume of reports on Applied Chemistry contain articles on fuels, dyes, glass, leather, pure chemicals, to mention only a selection. In almost every case there is the same tale to tell—reliance upon Germany for chemicals and chemical products of all descriptions up to 1914. Then desperate and on the whole extraordinarily successful efforts, undertaken out of sheer necessity, to make ourselves self-supporting, followed by hopes of the beginning of a period of national awakening and reconstruction. Wonders have already been done by the few, and it only remains for the many to recognise the importance of the work to be done and to bear their share of the burden. The author of the article on colouring matters and dyes, in an admirable survey of recent work in England, points out that "the existence of a well-organised coal-tar industry is one of the first essentials of national defence," and believes that the nation will come to recognise the fact that the synthetic dye question is in reality part of a much larger problem—that of the conservation of our resources in fuel. He thinks that in the future each nation will produce its own dyes and drugs, and there will be practically no international commerce in them. The article on acids, alkalis, and salts suggests some new sources of potash; *e.g.*, the old village sites in India, and the ash from weeds, hedge-clippings, and vegetable refuse. The papers on glass and on fine chemicals contain records of wonderful progress towards making up deficiencies in supplies, and although it goes without saying that there is still an enormous amount of uphill work to be done, on the whole we may be satisfied with the progress which is being made in the industrial applications of research work.

Memoirs and Proceedings of the Manchester Literary and Philosophical Society, 1915-1916. Vol. LX., Part III. Manchester: 36, George Street. Price 7s. 6d.

Readers of the Chemical News will probably find that the most interesting article in this volume is the one which comes first—"A *Résumé* of Work on the Bleach-out Process of Colour Photography," by John H. Smith. The author has done a large amount of investigational work on the subject, and although his researches have more or less come to a standstill owing to the war, he has already brought to light some important facts. Very little work on the subject has been published recently, and there is much need for the critical examination of several points. The volume, besides physical and geographical papers, contains a long and very interesting obituary notice of the late Sir Henry Enfield Roscoe.

Trattato di Chimica Analitica Applicata. ("Treatise on Applied Analytical Chemistry"). Volume II. By Prof. Vittorio Villavecchia, Milan: Ulrico Hoepli. Pp. xv+719. Price L.18,50. 1917.

Volume II. of this treatise contains detailed descriptions of methods of analysing and testing various alimentary products, such as meat, milk, sugar, &c.; also dyes, leathers and tanning materials, textile fibres, &c. Italian-speaking chemists will find that the treatise is the equal of any other of similar scope in any language, and the chemist who possesses a copy will have very little need of any other book of reference on analysis. The methods included for description are those which have been found the most accurate and expeditious in practice, and the instructions for carrying out the experimental work are very full and clear. Many diagrammatic and other illustrations are included, but the text is by no means overburdened with unnecessary pictures of apparatus. All tables that are likely to be required are given, and in the case of complicated calculations fully worked-out examples are provided.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 22, May 29, 1917.

Compounds of Zirconium with Sulphuric Acid.—Ed. Chauvenet.—Ten compounds of zirconium with sulphuric acid have been described, and the author has investigated the conditions of their existence. He made mixtures of zirconium and sulphuric acid of known composition, dried them at 200° so as to get them completely anhydrous, and then determined their densities, special precautions being taken to render the errors negligible. Thus he obtained proof of the existence of the following six compounds:—$Zr(SO_4)_2$, $Zr(SO_4)_2ZrO_2$, $5Zr(SO_4)_2.7ZrO_2$, $3Zr(SO_4)_2.5ZrO_2$, $Zr(SO_4)_2.2ZrO_2$, $Zr(SO_4)_2.3ZrO_2$. He could not obtain the other compounds which have been described.

No. 23, June 4, 1917.

This number contains no chemical matter.

Bulletin de la Société Chimique de France.
Vol. xxi.-xxii., No. 5, 1917.

Determination of Boric Acid in Special Glasses.—Paul Nicolardot and Jean Boudet.—The principle of the method employed by the authors to determine boric acid in glass is the same as that of the method described by Meurice, with certain special precautions. The boron is brought into solution as borate, the solution is neutralised, methyl-orange being used as indicator, and then glycerin or mannite is added, and the solution is titrated, using phenolphthalein. The most important modifications of the method are the methods adopted to ensure the complete solution of the boric acid and its titration in absence of CO_2. Ammoniacal salts are also driven off as they interfere with the action of phenolphthalein. It was found by control experiments that in these conditions all the boron could be determined, and magnesia and alumina, even in amounts exceeding those present in special glasses, do not affect the determination of boric acid.

MISCELLANEOUS.

Library Catalogue of Chemical Journals.—Owing to the great activity in chemical industries which has arisen during the last few years, the Council of the University, Liverpool, felt that a catalogue of current journals dealing with chemistry and chemical industries, and the libraries in which they could be found, would be of considerable value, and a committee was appointed last year to take this matter in hand. The work is not yet completed, but as a great deal has been done it may interest members to know the scope and present state of the catalogue. The list of chemical journals, about 5000 in number, comprises all those abstracted by the Society of Chemical Industry, Chemical Society, American Society (Chemical), Science Abstracts (Chemistry), or contained in the Patent Office Library, Royal Society Library, International Catalogue of Scientific Journals (Chemistry), Smithsonian Collection of Chemical Periodicals, and the Chemische Centralblatt. In addition, some thousands of journals dealing with textile, engineering, and other industries have been added, as these often contain articles of value to chemists, or are industries in which chemistry plays an important part. This list is now practically complete. About 800 libraries have been communicated with, and asked to send lists of the journals taken by them, or to mark on copies of our lists those contained in their libraries. This part of the work is steadily progressing, and the journals from our list which are to be found in over 200 libraries have been already catalogued. Patent specifications are also listed. Though the whole catalogue is not yet complete, members of the Society wishing to avail themselves of the lists and library data already collected, in order to find out the whereabouts of any particular journal which may not be taken in the library of their own town, will be given all available information on applying to Dr. A. Holt, Chemical Department, The University, Liverpool.

NOTES AND QUERIES.

⁂ Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Liquid Yeast.—I am desirous of obtaining a formula for the manufacture of a liquid yeast which could be produced at a minimum cost. If any kind correspondent will give a suggestion in this direction it will be greatly esteemed.—John J. Douglas.

THE CHEMICAL NEWS

Vol. CXVI., No. 3013.

THE COMPLEXITY OF THE CHEMICAL ELEMENTS.[*]

By Prof. FREDERICK SODDY, M.A., F.R.S.

(Continued from p. 75).

The Chemical Elements not Necessarily Homogeneous.

I pass now to the second and most novel sense in which the elements, or some of them at least, are complex. In their discovery of new radioactive elements, M. and Mme. Curie used radioactivity as a method of chemical analysis precisely as Bunsen and Kirchoff, and later Sir William Crookes, used spectrum analysis to discover caesium and rubidium, and thallium. The new method yielded at once, from uranium minerals, three new radio-elements, radium, polonium, and actinium. According to the theory of Sir Ernest Rutherford and myself, these elements are intermediate members in a long sequence of changes of the parent element uranium. In a mineral the various members of the series must co-exist in equilibrium, provided none succeed in escaping from the mineral, in quantities inversely proportional to their respective rates of change, or directly proportional to their periods of average life. Radium changes sufficiently slowly to accumulate in small but ponderable quantity in a uranium mineral, and so it wss shown to be a new member of the alkaline-earth family of elements, with atomic weight 226·0 occupying a vacant place in the Periodic Table. Polonium changes 4500 times more rapidly, and can only exist to the extent of a few hundredths of a milligrm. in a ton of uranium mineral. Actinium also, though its life period is still unknown, and very possibly is quite long, is scarce for another reason, that it is not in the main line of disintegration, but in a branch series which claims only a few per cent of the uranium atoms disintegrating. In spite of this, polonium and actinium have just as much right to be considered new elements, probably, as radium has. Polonium has great resemblances in chemical character both to bismuth and tellurium, but was separated from the first by Mme. Curie and from the second by Marckwald. In the position it occupies as the last member of the sulphur group, bismuth and tellurium are its neighbours in the Periodic Table. Actinium resembles the rare-earth elements, and most closely lanthanum, but an enrichment of the proportion of actinium from lanthanum has been effected by Giesel. The smallness of the quantities alone prevents their complete separation in the form of pure compounds as was done for radium.

The three gaseous members, the emanations of radium, actinium, and thorium, were put in their proper place in the Periodic Table almost as soon as radium was, for, being chemically inert gases, their characterisation was simple. They are the last members of the argon family, and the fact that there are three of about the same atomic weight was probably the first indication, although not clearly appreciated, that more than one chemical element could occupy the same place in the Periodic Table.

The extension of the three disintegration series proceeded apace; new members were being continually added, but no other new radio-elements—new, that is, in possessing a new chemical character—were discovered. The four longest-lived to be added, radio-lead or radium D, as it is now more precisely termed, and ionium in the uranium series, and mesothorium-I and radiothorium in the thorium series, could not be separated from other constituents always present in the minerals, radium-D from lead, ionium, and radio-thorium from thorium, and mesothorium I from radium. An appreciable proportion of the radioactivity of a uranium mineral is due to radium-D and its products, and its separation would have been a valuable technical achievement, but, though many attempts have been made, this has never been accomplished, and, we know now, probably never will be,

Seven years ago it was the general opinion in the then comparatively undeveloped knowledge of the chemistry of the radio-elements, that there was nothing especially remarkable in this. The chemist is familiar with many pairs or groups of elements, the separation of which is laborious and difficult, and the radio-chemist had not then fully appreciated the power of radioactive analysis in detecting a very slight change in the proportions of two elements, one or both of which were radioactive. The case is not at all like that of the rare-earth group of elements, for example, in which the equivalent or atomic weight is used as a guide to the progress of the separation. Here the total difference in the equivalent of the completely separated elements is only a very small percentage of the equivalent, and the separation must already have proceeded a long way before it can be ascertained.

Human nature plays its part in scientific advances, and the chemist is human like the rest. My own views on the matter developed with some speed when, in 1910, I came across a new case of this phenomenon. Trying to find out the chemical character of mesothorium I, which had been kept secret for technical reasons, I found it to have precisely the same chemical character as radium, a discovery which was made in the same year by Marckwald, and actually first published by him. I delayed my publication some months to complete a very careful fractional crystallisation of the barium-radium-mesothorium-I chloride separated from thorianite. Although a great number of fractionations were performed, and the radium was enriched, with regard to the barium, several hundred times, the ratio between the radium and mesothorium-I was, within the very small margin of error possible in careful radioactive measurements, not affected by the process. I felt justified in concluding from this case, and its analogy with the several other similar cases then known, that radium and mesothorium-I were non-separable by chemical processes, and had a chemical character not merely like but identical. It followed that some of the common elements might similarly be mixtures of chemically identical elements. In the cases cited, the non-separable pairs differ in atomic weight from 2 to 4 units. Hence the lack of any regular numerical relationships between the atomic weights would on this view follow naturally (*Trans. Chem. Soc.*, 1911, xcix., 72.) This idea was elaborated in the Chemical Society's Annual Report on Radioactivity for 1910, in the concluding section summing up the position at that time. This was I think the beginning of the conception of different elements identical chemically, which later came to be termed "isotopes," though it is sometimes attributed to K. Fajans, whose valuable contributions to radioactivity had not at that date commenced, and whose first contribution to this subject did not appear till 1913.

In the six or seven years that have elapsed the view has received complete vindication. Really, three distinct lines of sdvance converged to a common conclusion, and, so far as is possible, these may be disentangled. First, there has been the exact chemical characterisation from the new point of view of every one of the members of the three disintegration series, with lives over one minute. Secondly, came the sweeping generalisations in the interpretation of the Periodic Law. Lastly, there has been the first beginnings of our experimental knowledge of atomic structure, which got beyond the electronic constituents and at the material atom itself.

In pursuance of the first, Alexander Fleck, at my request, commenced a careful systematic study of the chemical character of all the radio-elements known o which our knowledge was lacking or imperfect, to see which were and which were not separable from known chemical elements. Seldom can the results of so much long and laborious chemical work be expressed in so few words. Every one, that it was possible to examine, was found to be chemically identical either with some common element or with another of the new radio-elements. Of the more important characterisations, mesothorium-II was found to be non-separable from actinium, radium-A from polonium, the three B-members and radium-D from lead, the three C-members and radium-E from bismuth, actinium-D and thorium-D from thallium. These results naturally took some time to complete, and became known fairly widely to others working in the subject before they were published, through A. S. Russell, an old student, who was then carrying on his investigations in radioactivity in Manchester. Their interpretation constitutes the second line of advance.

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[*] A Lecture delivered at the Royal Institution, May 18, 1917.

Before that is considered, it may first be said that every case of chemical non-separability put forward has stood the test of time, and all the many skilled workers who have pitted their chemical skill against Nature in this quest have merely confirmed it. The evidence at the present day is too numerous and detailed to recount. It comes from sources, such as in the technical extraction of mesothorium from monazite, where one process is repeated a nearly endless number of times; from trials of a very great variety of methods, as, for example, in the investigations on radium-D and lead by Paneth and von Hevesy; it is drawn from totally new methods, as in the beautiful proof by the same authors of the electro-chemical identity of these two isotopes; it is at the basis of the use of radioactive elements as indicators for studying the properties of a common element, isotopic with it, at concentrations too feeble to be otherwise dealt with, and from large numbers of isolated observations, as well as prolonged systematic researches. One of the finest examples of the latter kind of work, the Austrian researches on ionium, will be dealt with later. The most recent, which appeared last month, is by T. W. Richards and N. F. Hall, who subjected lead from Australian carnotite, containing therefore radium-D, to over a thousand fractional crystallisations in the form of chloride, without appreciably altering the atomic weight or the β-activity. So that it may be safely stated that no one who has ever really tested this conclusion now doubts it, and after all they alone have a right to an opinion.

This statement of the non-separability by chemical methods of pairs or groups of elements suffers perhaps from being in a negative form. It looks too much like a mere negative result, a failure, but in reality it is one of the most sweeping positive generalisations that could be made. Ionium we say is non-separable from thorium, but every chemist knows thorium is readily separated from every other known element. Hence, one now knows every detail of the chemistry of the vast majority of these new radio-elements by proxy, even when their life is to be measured in minutes or seconds, as completely as if they were obtainable, like thorium is, by the ton. The difference it makes can only be appreciated by those who have lived through earlier days, when, in some cases, dealing with the separation of radio-constituents from complex minerals, after every chemical separation one took the separated parts to the electroscope to find out where the desired constituent was.

As the evidence accumulated that we had to deal here with something new and fundamental, the question naturally arose whether the spectrum of isotopes would be the same. The spectrum is known, like the chemical character, to be an electronic rather than mass phenomenon, and it was to be expected that the identity should extend to the spectrum. The question has been tested very thoroughly by A. S. Russell and R. Rossi in this country, and by the Austrian workers at the Radium Institut of Vienna, for ionium and thorium, and by various workers for the various isotopes of lead. No certain difference has been found, and it may be concluded that the spectra of isotopes are identical. This identity probably extends to the X-ray spectra, Rutherford and Andrada having shown that the spectrum of the γ-rays of radium-B is identical with the X-ray spectrum of its isotope, lead.

The Periodic Law and Radioactive Change.

The second line of advance interprets the Periodic Law. It began in 1911 with the observation that the product of an α ray change always occupied a place in the Periodic Table two places removed from the parent in the direction of diminishing mass, and that in subsequent changes where α-rays are not expelled the product frequently reverts in chemical character to that of the parent, though its atomic weight is reduced 4 units by the loss of the α-particle, making the passage across the table curiously alternating. Thus the product of radium (Group II.) by an α-ray change is the emanation in the zero group, of ionium (Group IV.), radium, and so on, while, in the thorium series, thorium (Group IV.) produces by an α-ray change mesothorium-I (Group II.), which, in subsequent changes in which no α-rays are expelled, yields radiothorium, back in Group IV. again. ("Chemistry of the Radio-Elements," p. 29, 1st Edition, 1911.) Nothing at that time could be said about β ray changes. The products were for the most part very short lived and imperfectly characterised chemically, and several lacunæ still existed in the series masking the simplicity of the process. But early in 1913 the whole scheme became clear, and was pointed out first by A. S. Russell, in a slightly imperfect form, independently by K. Fajans from electro-chemical evidence, and by myself, in full knowledge of Fleck's results, still for the most part unpublished, all within the same month of February. It was found that, making the assumption that uranium-X was in reality two successive products giving β-rays, a prediction Fajans and Göhring proved to be correct within a month, and a slight alteration in the order at the beginning of the uranium series, every α-ray change produced a shift of place as described, and every β ray change a shift of one place in the opposite direction. Further and most significantly, when the successive members of the three disintegration series were put in the places in the table dictated by these two rules, it was found that all the elements occupying the same place were those which had been found to be non-separable by chemical processes from one another, and from the element already occupying that place, if it was occupied, before the discovery of radioactivity. For this reason the term "isotope" was coined to express an element chemically non separable from the other, the term signifying "the same place."

So arranged, the three series extended from uranium to thallium, and the ultimate product of each series occupied the place occupied by the element lead. The ultimate products of thorium should, because six α-particles are expelled in the process, have an atomic weight 24 units less than the parent, or about 208. The main ultimate product of uranium, since eight α-particles are expelled in this case, should have the atomic weight 206. The atomic weight of ordinary lead is 207·2, which made it appear very likely that ordinary lead was a mixture of the two isotopes, derived from uranium and thorium. The prediction followed that lead, separated from a thorium mineral, should have an atomic weight about a unit higher, and that separated from uranium minerals about a unit lower, than the atomic weight of common lead, and in each case this has now been satisfactorily established.

The Atomic Weight of Lead from Radioactive Minerals.

It should be said that Boltwood and also Holmes had, from geological evidence, both decided definitely against it being possible that lead was a product of thorium, because thorium minerals contained too little lead, in proportion to the thorium, to accord with their geological ages. Whereas, the conclusion that lead was the ultimate product of the uranium series had been thoroughly established by geological evidence, and has been the means, in the hands of skilful investigators, of ascertaining geological ages with a degree of precision not hitherto possible. Fortunately I was not deterred by the *non possumus*, for it looks as if everybody was right! An explanation of this paradox will later be attempted. In point of fact, there are exceedingly few thorium minerals that do not contain uranium, and since the rate of change of uranium is about 2·6 times that of thorium, one part of uranium is equal as a lead-producer to 2·6 parts of thorium. Thus Ceylon thorianite, one of the richest of thorium minerals, containing 60 to 70 per cent of ThO_2, may contain 10 to 20 and even 30 per cent of U_3O_8, and the lead from it may be expected to consist of very similar quantities of the two isotopes, to be in fact very similar to ordinary lead. I know of only one mineral which is suitable for this test. It was discovered at the same time as thorianite, and from the same locality—Ceylon thorite, a hydrated silicate containing some 57 per cent of thorium and 1 per cent of uranium only. In the original analysis no lead was recorded, but I found it contained 0·4 per cent, which, if it were derived from uranium only, would indicate a very hoary ancestry, comparable, indeed, with the period of average life of uranium itself. On the other hand, if (1) all the lead is of radioactive origin, (2) is stable, and (3) is derived from both constituents, as the generalisation being discussed indicated, this 0·4 per cent of lead should consist of 95·5 per cent of the thorium isotope and 4·5 per cent of the uranium isotope. Thorite thus offered an extremely favourable case for examination.

In preliminary experiments in conjunction with H. Hyman, in which only a grm. or less of the lead was available, the atomic weight was found relatively to ordinary lead to be perceptibly higher, and the difference, rather less than one-half per cent, was of the expected order.

I was so fortunate as to secure a lot of 30 kilos. of this unique mineral, which was first carefully sorted, piece by piece, from admixed thorianite and doubtful specimens. From the 20 kilos. of first grade thorite, the lead was separated, purified, reduced to metal, and cast *in vacuo* into a cylinder, and its density determined together with that of a cylinder of common lead similarly purified and prepared. Sir Ernest Rutherford's theory of atomic structure, to be dealt with in the latter part of this discourse, and the whole of our knowledge as to what isotopes were, made it appear probable that their atomic volumes, like their chemical character and spectra, should be identical, and therefore that their density should be proportional to their atomic weight. The thorite lead proved to be 0·26 per cent denser than the common lead. Taking the figure 207·2 for the atomic weight of common lead, the calculated atomic weight of the specimen should be 207·74.

The two specimens of lead were fractionally distilled *in vacuo*, and a comparison of the atomic weights of the two middle fractions made by a development of one of Stas's methods. The lead was converted into nitrate in a quartz vessel, and then into chloride by a current of hydrogen chloride, in which it was heated at gradually increasing temperature to constant weight. Only single determinations have been done, and they gave the values 207·20 for ordinary lead, and 207·694 for the thorite lead, figures that are in the ratio of 100 to 100·24. This, therefore, favoured the conclusion that the atomic volume of isotopes is constant.

At the request of Mr. Lawson, interned in Austria, and continuing his researches at the Radium Institut under Prof. Stefan Meyer, the first fraction of the distilled thorite lead was sent him, so that the work could be checked. He reports that Prof. Hönigschmid has carried through an atomic weight determination by the silver method, obtaining the value 207·77 ± 0·014, as the mean of eight determinations.[*] Hence, the conclusion that the atomic weight of lead derived from thorite is higher than that of common lead, has been put beyond reasonable doubt.

Practically simultaneously with the first announcement of these results for thorium lead, a series of investigations were published on the atomic weight of lead from uranium minerals, by T. W. Richards and collaborators at Harvard, Maurice Curie in Paris, and Hönigschmid and collaborators in Vienna, which show that the atomic weight is lower than that of ordinary lead. The lowest result hitherto obtained is 206·046, by Hönigschmid and M'le. Horovitz for the lead from the very pure crystallised pitchblende from Morogoro (German East Africa), whilst Richards and Wadsworth obtained 206·085 for a carefully selected specimen of Norwegian clevite. Numerous other results have been obtained, as, for example, 206·405 for lead from Joachimsthal pitchblende, 206·82 for lead from Ceylon thorianite, 207·08 for lead from monazite, the two latter being mixed uranium and thorium minerals. But the essential proportion between the two elements has not unfortunately been determined. Richards and Wadsworth have also examined the density of their uranium lead. In every case they have been able to confirm the conclusion that the atomic volume of isotopes is constant, the uranium lead being as much lighter as its atomic weight is smaller than common lead. Many careful investigations of the spectra of these varieties of lead show that the spectrum is absolutely the same so far as can be seen.

(To be continued).

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

Part I.—Solids.

By IRVING LANGMUIR.

(Continued from p. 81).

Chemical Compounds Existing Only in the Solid State.—From what has been said regarding the relation between primary and secondary valences in solid bodies, it would follow that in general the composition of a solid body should give us little or no information about the primary valences. Conversely, we should expect more compounds to exist in the solid state than we would be led to predict from the ordinary rules of valence.

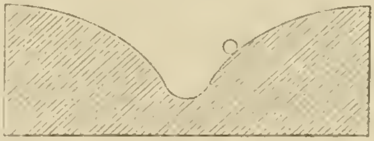

Fig. 1.

When we consider that every atom (and every molecule for that matter) is surrounded by a field of electro-magnetic force, it appears probable that solids can be built up with almost any arrangement of atoms, provided the temperature is sufficiently low. If these arrangements of atoms are regular so as to constitute a space lattice, the resulting solid will have a definite and invariable chemical composition which can be represented by a chemical formula, and would, therefore, be recognised as a chemical compound. The arrangement of the atoms in such compounds would bear no more relationship to the primary valence of the atoms than does the arrangement of the carbon, oxygen, and calcium atoms in a crystal of calcite. The formula representing a compound of this type would thus be totally unrelated to the valence of the atoms.

The reason that the composition of solid compounds is so often consistent with the ordinary valence rules, is probably that the compounds are formed from solutions or from gaseous phases. In liquids or gases there is naturally more opportunity for the primary valences to manifest themselves.

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* From the *Journal of the American Chemical Society*, xxxviii. No. 11.

As a matter of fact there are vast members of chemical compounds which exist in the solid state only, and among these compounds the absence of valence relations is very striking.

Tammann and his students have proven the existence of a hundred or more definite metallic compounds by their studies of alloys. Out of 100 such compounds only 26 have formulas which agree with the ordinary valence (Tammann, *Zeit. Anorg. Chem.*, 1906, xlix., 113; and 1907, lv., 289). A few typical compounds are: $AgMg_3$ $AgMg$, $AuZn$, Au_3Zn_5, Cu_3Al, $CuAl$, $CuAl_2$, Mg_4Al_3, $AlSb$, Zn_7Fe, Zn_3Fe, Al_5Fe_2, $NaZn_{12}$, $NaCd_5$, $NaHg_4$, $NiCd_5$, $AuSb_2$, &c. Tammann shows that definite compounds are never formed between metals which are closely related in the periodic system, such as Cu-Ag or Fe-Ni, although solid solutions or mixed crystals frequently form in these cases.

If we consider these metallic compounds from the viewpoint we have developed above, it is evident that the atoms are held together by secondary valence, as are, for instance, those in a copper crystal or a rock-salt crystal. The reason that they have a definite chemical composition is that the atoms are arranged in some form of regular lattice. For example, if, in a face-centered cubic lattice such as that of a copper crystal, we should replace the corner atoms by atoms of an element A, and replace the atoms in the faces of the cubes by atoms B, then we should have a compound of the composition AB_3. Each atom A would be surrounded by 12 atoms B all equidistant. Each atom B, however, would have four atoms of A and 8 of B equidistant from it. Such a structure would reveal nothing as to the valency of the atoms. It is quite probable that the compound $AgMg_3$ has a structure of this kind.

If the atoms of the copper crystal we have considered should be replaced by atoms of two elements A and B in an irregular manner, then the resulting crystal would not have a definite chemical composition and would, therefore, not be recognised as a chemical compound, but would be considered a solid solution or mixed crystal. Yet there is no reason to assume that the forces holding the crystal together in one case are any different from those in the other.

If the two elements have combined together to form a chemical compound in one case, why not assume that the elements are equally combined in the mixed crystal? In the crystal of a pure metal we should also consider the atoms chemically combined with one another.

In mixed crystals, or solid solutions, the atoms are evidently arranged in a haphazard manner according to the laws of probability, many different arrangements of atoms occurring side by side in the crystal. If the atoms of the two elements differ sufficiently in size or in their fields of force, then certain of these arrangements will be more stable than others. Thus, although at low temperatures almost any conceivable arrangement of atoms might be stable, it may be impossible to form mixed crystals by cooling a molten mass, because the atoms during the process of solidification have ample opportunity to arrange themselves in the most stable arrangements.

Thus the limitation in the number of compounds actually found is probably due to the restrictions imposed by our present methods of preparing these alloys by solidification from a melt, and is not an indication that such chemical compounds (or solid solutions) are not capable of existence in the solid condition.

Mineralogy also affords us an abundance of compounds which exist in the solid condition only, and whose composition is not in accordance with the ordinary valence rules. The complex silicates are apparently built up of compounds of the first order (SiO_2, K_2O, Al_2O_3, H_2O, &c.) in much the same way that the metallic compounds are built up of the atoms of the metals, If we consider such typical compounds as $(K_2O)(Al_2O_3)(SiO_2)_6$; $(MgO)_3(SiO_2)_4$-(H_2O); $(MgO)(SiO_2)(2H_2O)_2$, &c., it appears that the number of each of the groups (K_2O), (Al_2O_3), &c., which enter into the formula bears no relation to the valence of the elements. It is probable that in many cases each of the groups K_2O, Al_2O_3 really constitute group molecules, and that these are held together in the crystal by secondary valence, just as the atoms of the metallic compounds are.

Solid solutions or mixed crystals are of even more frequent occurrence among minerals than among alloys, and similar considerations must apply in regard to their constitution.

In the field of inorganic chemistry, especially in that of complex salts so well covered by Werner and his students, the relative number of compounds that can exist in the gaseous condition is extremely small.

Practically all complex compounds decompose or dissociate when heated. Even sulphuric acid gives a vapour whose density indicates that it is completely dissociated into H_2O and SO_3. In fact the great majority of complex compounds do not even show a molecular weight in solution which corresponds to their composition in the solid state. For example, when alum $(K_2O)(Al_2O_3)(SO_3)_4(H_2O)_{24}$ is dissolved in water, it shows a "molecular weight" very much less than that corresponding to its formula. Crystals containing water of crystallisation cannot be made to evaporate and still retain the combined water.

The number of complex compounds that can be formed must be unlimited. If methods can be found for forming them at sufficiently low temperature, probably almost any conceivable arrangements of group molecules could be built up having definite chemical compositions. Or solid solutions consisting of almost any combination of atoms and molecules could theoretically be formed. We are only sharply restricted in the formation of compounds in the case of compounds of the first order. But there is no sharp limit to the compounds that may be formed by secondary valences.

So far we have considered only crystalline solid bodies. It is evident that atoms or group molecules could be arranged irregularly in space (not according to a regular space lattice). A solid body built up in this way would have the properties of an amorphous body or glass. There can be little reasonable doubt but that the structure of glass is of this nature. Such a structure is naturally much more easily built up of group molecules than of atoms, for the greater symmetry of the atom enables it to assume definite and regular positions with respect to its neighbours more readily than group molecules could do.

The nature of the forces acting between the atoms or group molecules in amorphous bodies cannot be essentially different from that in crystals. We should expect the union between adjacent atoms or molecules to be dependent upon exactly the same kind of chemical properties as those which determine the combination of the atoms or molecules to form complex compounds (secondary valence).

From the fact that glasses, when heated, change to the liquid state by a continuous process, we are led to conclude that the structure of a liquid does not differ from that of a glass in any essential respect except that in the liquid there is a certain mobility (entirely analogous to tautomerism). Therefore, even in a liquid we look upon every atom (or group molecule) as combined chemically (or adsorbed) to all the adjacent ones. The molecular weight is, therefore, a term that has very little significance in the case of a liquid. This theory of the structure of liquids will be developed in more detail in the second part of this paper.

Structure of the Surfaces of Solids.

Unfortunately the study of crystals by the X-ray spectrum has not yet given us any direct knowledge of the structure of the surfaces of solids. From the point of view of the chemist, the structure of the surface must be of the utmost importance, for chemical reactions in which solids take part are practically always surface reactions.

TABLE I.

Metal.	K. C. G. S. units.	λ ergs.	A/ρ.	$\sqrt[3]{1+\Delta V_0}$.	σ cm.	$\Delta\sigma$ cm.
W	$0·28 \times 10^{-12}$	$9·2 \times 10^{12}$	9·6	1·20	$2·8 \times 10^{-8}$	$0·57 \times 10^{-8}$
Pt	$0·38 \times 10^{-12}$	$5·4 \times 10^{12}$	9·1	1·19	$2·78 \times 10^{-8}$	$0·53 \times 10^{-8}$
Mo	$0·46 \times 10^{-12}$	$7·4 \times 10^{12}$	11·1	1·21	$2·96 \times 10^{-8}$	$0·62 \times 10^{-8}$
Hg	$3·95 \times 10^{-12}$	$0·58 \times 10^{12}$	14·8	1·16	$3·26 \times 10^{-8}$	$0·52 \times 10^{-8}$
Cs	$61·0 \times 10^{-12}$	$1·0 \times 10^{12}$	71·0	1·12	$5·50 \times 10^{-8}$	$0·66 \times 10^{-8}$

Our knowledge of the surfaces of solids must, therefore, be derived from indirect sources.

Since the forces that hold the atoms of solids together are of the same kind as those that hold the atoms of complex chemical compounds, we have excellent reasons for believing that the forces decrease extremely rapidly as the distance between atoms increases. We may also draw this conclusion from the compressibility of solids.

The energy which must be expended in separating the atoms of a solid metal from each other is given by the latent heat of evaporation λ (per grm.-atom). We can also calculate the energy necessary to change the distance between atoms from the compressibility. By comparing this energy with the latent heat, we may estimate the distance through which atomic forces are effective.

Let K represent the coefficient of compressibility of an element having an atomic volume A/ρ. We have good reasons for believing that the atoms of a solid are subject to forces that vary in proportion to the displacement of the atoms from their equilibrium positions (see Note).

(NOTE.—The specific heats and other properties of the heavier elements compel us to this view when the displacements are small. Richards has shown that the compressibility of the elements decreases gradually as the pressure is raised to very high values. This proves that the repulsive forces between atoms increase more rapidly than the displacement. It is well known that liquids can be subjected to negative pressures and have substantially the same coefficient of compressibility for negative as for positive pressures. Undoubtedly the coefficient K should increase considerably for very intense negative pressures. Nevertheless the assumption of a constant value of K could hardly affect the order of magnitude *of the calculated* range of atomic forces).

If we compress a unit volume of a solid so as to decrease its volume by the amount ΔV, the work expended will be $(\Delta V)_2/2K$. If the body is subjected to tension in all directions (negative pressure) so as to *increase* its volume by the amount ΔV, the work expended will also be $(\Delta V)_2/2K$. This relation will hold accurately only for such small negative pressures that K remains constant. It is evident that as the atoms are being separated from each other, the attractive forces will at first increase in proportion to the displacement, then gradually more slowly, until finally the attractive force reaches a maximum. Beyond this distance the force rapidly decreases (probably according to about the inverse 4th or 5th power) to negligible values. It will be very instructive, however, to calculate on the assumption that K is constant, how far we need to pull the atoms apart before the work expended will equal the known latent heat of evaporation.

We readily obtain—

$$(\Delta V_0)^2 = \frac{2\lambda K}{A/\rho}.$$

In this equation ΔV_0 represents the increase in volume which could cause an expenditure of energy equal to λ per grm.-atom. The volume is thus increased from 1 to $1 + \Delta V_0$. The relative increase in the distance between the atoms is given by $\sqrt[3]{1 + \Delta V_0}$. In Table I. the data for several elements are given. According to Richards, tungsten is the least compressible and caesium the most compressible metal.

Thus, if the attractive forces between the atoms varied in proportion to the displacement, the expenditure of energy necessary to increase the distance between the atoms by 12 per cent in case of caesium (or 21 per cent in case of molybdenum) would be as great as that actually required to separate them to an infinite distance.

Actually, the attractive force can vary proportionally to the displacement only for displacements much less than 10 per cent of the distance between atoms. However, the distance calculated by the above rough method is probably very close to that at which the *maximum attractive force* occurs. The work done in separating the atoms beyond this distance probably compensates for the decrease in attractive force before the maximum is reached.

From these considerations it seems safe to say that: *The attractive force between atoms reaches a maximum when the atoms are separated by distances 10-30 per cent greater than the distance at which they are in stable equilibrium.* (Grüneisen, *Ann. Physik*, 1912, xxxix., 298, by a mathematical development of a theory of monoatomic solids, concludes that the average *amplitude of vibration* of the atoms in a solid at its melting point is 8·5 per cent of the distance between the atoms). Since the force varies with a high power of the distance, we may also conclude: *The attractive force becomes practically negligible when the distance between the centres of the atoms becomes twice as great as the distance at which the atoms are in equilibrium.* (Probably the best evidence of the very limited range of atomic forces is that afforded by surface tension phenomena. This will be discussed in the second part of the paper).

It is interesting to note in Table I. that the values of $\sqrt[3]{1 + \Delta V_0}$ are largest for the elements of smallest atomic volume. This suggests that the increase in actual distance at which the attractive force becomes a maximum may be approximately the same for all the elements. In the sixth column are given the distances between the centres of the atoms calculated from the atomic volume on the assumption that the atoms are arranged according to a face-centered cubic lattice. The next column gives $\Delta\sigma$, the increase in this distance corresponding to the increase in volume represented by $1 + \Delta V_0$. It is seen that the values of $\Delta\sigma$ are substantially constant, so that we may conclude that: *The attractive forces between atoms increase to a maximum when the distance between the atoms is about $0·6 \times 10^{-8}$ cm. greater than the distance at which the attractive force is zero.*

We are now in a position to draw certain conclusions regarding the structure of the surfaces of crystals.

Let us consider a crystal such as calcite in which cleavage surfaces may be obtained. To break a crystal into two parts requires the expenditure of a certain amount of energy. Let γ be the *work* or *free energy* which must be expended in producing each square centimetre of cleavage surface. Thus if we have a crystal of one square centimetre in cross-section (parallel to a cleavage face), γ will be one-half of the work required to separate the crystal into two parts. In general γ will decrease as the temperature rises. If we consider the mechanism of the formation of a cleavage surface, it is evident that as the atoms are pulled away from each other a certain amount of work will be done by the thermal agitations of the atoms. The atoms moving towards the receding surface are repelled by a gradually decreasing force, so that they return from the receding surface with a velocity lower (on the average) than that with which they started out. Thus there must be a certain cooling effect accompanying the formation of a cleavage surface, and this heat energy must result in a corresponding decrease in the free energy required to produce the surface. This reasoning is entirely analogous to that in the case of the mechanism of the adiabatic expansion of a gas.

Simple thermodynamical reasoning (see first chapter of Nernst's "Theoretical Chemistry") shows that in the production of a cleavage surface the amount of energy contributed by the thermal agitation is equal to $-T\,d\gamma/dT$. If we add to this the free energy expended, we obtain, for the total energy involved in the formation of a unit surface, the expression—

$$\gamma_0 = \gamma - T\frac{d\gamma}{dT}. \qquad (2)$$

This quantity γ_0 represents the total potential energy of the surface. Since we look upon atomic forces as electromagnetic in nature, the quantity γ_0 is a quantitative measure of the increase in the energy of the electromagnetic field surrounding the atoms, produced by the formation of the surface.

Just as we traced a relationship between the compressibility, the heat of vaporisation, and the range of atomic forces, we may derive a similar relationship between the elastic properties, surface energy, and range of atomic forces. Unfortunately, however, few data on the surface energy of solids are available.

There is every reason for believing that the range of atomic forces is of the same order of magnitude in all the states of matter. In forming a cleavage surface, therefore, it is probable that the atoms pull part when the distance between adjacent atoms has been increased by about $0{\cdot}6 \times 10^{-8}$ cm. (Further evidence in support of this statement will be given in the second part of this paper).

When electrically charged or magnetised bodies are brought into proximity, they tend to move in such a way that the total energy of the electric or magnetic field becomes a minimum. For example, if we imagine a number of small horseshoe magnets to be placed in a box and shaken, we should expect on opening the box to find that the magnets had become attached to each other in pairs in such a way that in each pair the north pole of one is in contact with the south pole of the other. This arrangement would be a very stable one and would require a maximum amount of energy to break it up.

In a similar manner the atoms in the surface of a crystal must tend to arrange themselves so that the total energy in the field surrounding them will be a minimum (see Note). In general, this will involve a shifting of the positions of the atoms with respect to one another. However, from the fact that energy is always required to separate a solid body into two parts we must conclude that the field energy associated with the surface atoms is always greater than that associated with a like number of atoms in the interior of the solid, notwithstanding the shifting of the positions of the atoms in the surface layer.

(Note.—In the second part of this paper it will be shown that this principle is of great importance in connection with surface tension phenomena. The group molecules in liquids arrange themselves in the surface layer in such a way that the part of the molecule which has the weakest field around it actually forms the surface, while the more active parts of the molecule are drawn below the surface, and are then without effect on the surface tension except in so far as they crowd the surface atoms apart. The above principle also seems to be related to the cleavage or crystal habits of solids. In a crystal built up of atoms arranged according to a face centred cubic lattice the number of atoms per sq. cm. of crystal face is $5{\cdot}56 \times 10^{15} \times V^{-2/3}$ for the 1 : 0 : 0 faces, $4{\cdot}02 \times 10^{15} \times V^{-2/3}$ for the 1 : 1 : 0 faces, and $6{\cdot}57 \times 10^{15} V^{-2/3}$ for the 1 : 1 : 1 faces. Here V is the atomic volume. Thus the atoms are arranged more compactly in the octahedron faces than in any others. For such faces the value of γ_0 should be a minimum. When platinum is slowly sublimed at high temperatures, as, for instance, in the winding of an electric furnace, it crystallises in the form of beautiful octahedra. The writer has observed similar crystals of tungsten. On the other hand, in the simple cubic lattice the most compact arrangement of the surface atoms occurs in the 1 : 0 : 0 faces. Crystals of the alkali halides have cubic cleavage and usually crystallise as cubes, and the *atoms* in these crystals are spaced according to a simple cubic lattice).

The smallness of the range of the atomic forces compels us to conclude that in general the distances through which the surface atoms are shifted from their original positions in the solid are small compared to the average distance between atoms. We must also conclude that the abnormal surface arrangement is usually limited to the surface layer only.

The surface of a solid (or liquid) therefore does not contain, as is usually assumed, a transition layer, consisting of several layers of atoms or "molecules," in which the density varies by continuous gradations from that of the solid to that of the surrounding gas or vapour. Instead we find that the change from solid to empty space is most abrupt. In a sense the rearrangment of the atoms in the surface layer causes this layer to assume the character of a transition layer, but the density of the packing of the atoms in this layer is undoubtedly greater than in the body of the solid, so that there can be no gradual change in density from that of the solid to that of the space. Additional evidence in favour of this view will be given in the remainder of this paper.

The surface of a crystal must then consist of an arrangement of atoms as definite as that existing in the interior of the crystal, although slightly different from the latter. The surface must thus be looked upon as a sort of checker board containing a definite number of atoms, of definite kinds arranged in a *plane* lattice formation. The space between and immediately above (away from the interior) these atoms is surrounded by a field of electro-magnetic force more intense than that between the atoms inside the crystal.

There are good reasons for believing that the intensity of this surface field of force is substantially independent of the temperature. The energy in the surface field is measured by γ_0 (Equation 2). Now the work done, during the formation of a fresh surface by the thermal agitation of the molecules (namely, $-T\,d\gamma/dT$), should be approximately proportional to the temperature. Therefore, $d\gamma/dT$ should be independent of the temperature. Thus we may place—

$$\gamma = a - bT \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

where a and b are constants. Combining this with (2) we find $\gamma_0 = a$. In other words, γ_0, the total energy of the electro-magnetic surface field, should be independent of temperature.

In the case of liquids the free energy necessary for the formation of unit surface is called the surface tension. By analogy we would be justified in calling γ the surface tension of the solid. However, on the whole, it seems perferable with both solids and liquids to refer to the quantity γ as the *free surface energy* and γ_0 as the *total surface energy*.

(To be continued).

EXAMINING COMMERCIAL BROMINE.

By ELWYN WALLER.

Recently a sample of commercial bromine was brought to the writer's laboratory for examination. The impurities likely to be present are not very numerous. If the material has been recovered from by-products in the manufacture of substances from aromatic and other organic compounds, a material amount of organic substance may be present, *e.g.*, Reymann (*Ber.*, viii., 792) mentions finding 10 per cent bromoform in one case. Ordinarily, only a small amount of grease, wax, or paraffin, which has been used in sealing the container, is all of the organic impurity present. The presence of SO_3 or H_2SO_4 is possible, but the amount is usually insignificant. The presence of Br hydrates may perhaps occur, but that branch of the subject does not seem to have been investigated. The occurrence of Cl is naturally the chief impurity, both on account of the association in nature and also on account of the usual methods of manufacture.

In testing, some manufacturers determine the purity by taking the specific gravity in a specially constructed apparatus, and by reference to a table (made up, I know not how) read off what they claim is the true per cent of Br in the sample. Apparently it is assumed, in the construction of the table, that Cl is the only impurity. The possible influence of other impurities would seem to render this method a rather uncertain one, especially as the authorities are not altogether in accord, varying from 2·966 to 3·1872 (judging from the statements in Watts' Dictionary, i., 676).

The sample referred to showed

sp. gr.	at 5·6° C. ..	3·0286
	at 25° C. ..	3·0135
A sample marked C.P. from a well-known dealer	at 25° C. ..	3·1021

Titration of a known quantity with standard $Na_2S_2O_3$, is one method recommended by many. The objection to it is that this permits of working on only a small quantity, and the assumption must also be made that only Br and Cl are present.

Friedheim and Meyer (*Z. Anorg. Chem.*, i., 407) suggests the application of Dechan's process (*Journ. Chem. Soc.*, xlix., 682), which was devised for the examination of brines, mineral waters, &c. It depends on the following: With a mixture of bromides and chlorides, addition of a large excess of $K_2Cr_2O_7$ and positive acidification with H_2SO_4, on boiling gives off Br but no Cl unless it is allowed to become very concentrated, when CrO_2Cl_2 may distil over. By the aid of a current of steam passed through the boiling solution, all the Br can be driven into the distillate, and in the residual solution the Cl can be determined with $AgNO_3$. To apply the process in the case of commercial Br, 0·5 to 1 grm. of the sample is weighed out in a thin glass bulb, which is broken under the surface of NaOH solution. When all Br has been taken up, 50 cc. of a 3 per cent solution of H_2O_2 is added, and the excess boiled out. Transfer to a distilling flask, add 10 grms. $K_2Cr_2O_7$ in crystals and 20 cc. H_2SO_4 (1 : 1 by vol.). Distil until the distillate gives no reaction for Br, avoiding a concentration beyond what would be equivalent to 8 cc. concentrated H_2SO_4 in 100 cc. of liquid. Then dilute the contents of the flask and precipitate an aliquot portion with $AgNO_3$.

The process was tried but proved unsatisfactory. To obtain the necessary reagents absolutely free from chlorides is, at this time especially, a difficult matter. It was also found that unless the concentration is brought to a certain point, no Br whatever will distil over, though much still remains, consequently constant attention is necessary to keep the degree of concentration in the flask between the proper limits. The results obtained were irregular and not concordant.

Erchenbrecher (*Z. Angew. Chem.*, 1894, 636) treats 6 grms. of the sample with 25 cc. of $N/5$ solution of KBr or NaBr, evaporates on the water-bath, finally in a weighed dish, ignites gently and weighs. The Cl of the sample displaces the Br of the salt, and by the use of a table the proportion may be found.

To weigh out precisely 6 grms. or any other prescribed quantity of Br is a troublesome operation, so that the use of a table would hardly seem to be of advantage in this connection. The principle involved can, however, be applied as will be seen later.

Kubierschky (*loc. cit.*) applies the same principle by shaking 25 cc. of the sample in a flask with 25 cc. of N KBr, settling and taking the specific gravity of the supernatant aqueous solution. With pure Br he states the specific gravity should be 1·227, and he has made a table showing the gravities corresponding to different percentages of Cl.

The application of the above principle proved to be a convenient mode of conducting the test. The method pursued was to weigh out 6 to 8 grms. of the sample in a small stoppered flask. This was then poured and rinsed into a 350 cc. beaker containing about 70 cc. of water. The object in using so large a beaker was to avoid loss when boiling out the Br. To this was then added, by means of a pipette, 20 or 25 cc. of a solution of pure NaBr of 7 to 10 per cent strength. At the same time, *using the same pipette*, the same amount of NaBr solution was pipetted into a weighed dish to serve as a blank.

The beaker containing the Br was placed on the boiling water-bath, and allowed to remain there until the Br had all boiled off, and most or all of it had been expelled from the solution, when the solution of mixed bromide and chloride was transferred to another weighed dish, and both that and the blank were evaporated to dryness, the last traces of moisture expelled by heating in air-bath at about 130°, ignited gently and weighed. The salts obtained from the "mixed" is less than that from the "blank" by an amount equivalent to the difference between the combining weights of Cl and Br.

In other words, Blank — Mixed = Diff., and since

(Br) 79·92 — (Cl) 35·46 = 44·46
44·46 : 35·46 = Diff. : Cl present.

For most purposes, 80 per cent of the difference in weights give the Cl.

The contents of the dishes should be dissolved separately, and each diluted to some convenient bulk (say 250 cc.), and aliquot portions tested by titration with standard $AgNO_3$. The halogen equivalent in the two masses of salts should be the same if no losses have occurred.

Applied to the sample submitted the results were :—

Taken.	Wt. of "Blank."	Wt. of "Mixed."	Diff.	= Cl.	Per cent Cl.
6·7249	1·5884	1·3206	0·2678	0·21364	3·18
7·2330	1·3983	1·1257	0·2726	0·21747	3·06
8·4340	2·0737	1·7434	0·3303	0·26349	3·12

Material from a dealer in laboratory supplies marked as Bromine C.P. was found to contain 0·19 per cent Cl. —*Journal of Industrial and Engineering Chemistry*, viii., 837.

GRANULAR CALCIUM CHLORIDE AS A DRYING AGENT.

By A. T. McPHERSON.

IN measuring the efficiency of calcium chloride as a drying agent, Baxter and Starkweather employed the fused salt (*Journ. Am, Chem. Soc.*, 1916, xxxviii., 2038). However, granular calcium chloride is much more commonly used, and is more rapid and efficient because its desiccating action is due to adsorption rather than to hydration, as is the case with the fused salt. Since the vapour pressure of an adsorbing substance is a function of the surface moisture that it already contains, it would be expected that granular chloride of calcium, when absolutely dry, would remove every trace of moisture from a gas passed over a sufficiently long column of it. Our experiments show this to be the case.

The method employed was to aspirate air containing a known amount of water-vapour over a long column of absolutely anhydrous granular calcium chloride, and absorb and weigh the residual moisture in a glass stoppered phosphorus pentoxide tube. To obtain the anhydrous chloride a tube containing a column of the chemically pure salt 100 cm. long and 2 cm. in diameter which was used for subsequent experiments was heated to 260–275° in a current of air dried over phosphorus pentoxide (*cf.* Abegg, "Handbuch der Anorganischen Chemie," ii., 98). Dry carbon dioxide was passed through for some time to neutralise any traces of oxide that may have been produced by hydrolysis. A sample of calcium chloride removed from the tube at the close of the experiment gave a clear solution that was neutral to litmus. The tube was placed in a thermostat at 25°, air saturated with water vapour aspirated through, and the pentoxide tube weighed at intervals, with the following results:—

EXPERIMENT I.

Temperature	25						
Litres per hour	9·4	9·5	9·5	7·7	9·0	9·0	9·5
Litres of air	33·9	42·9	46·4	46·1	46·4	46·9	45·2
Mgrm. of residual water-vapour . ..	+0·1	0·0	+0·2	+2·2	+5·5	+7·1	+9·2

Volume of air dried with maximum efficiency, 123 litres.

Since the purpose of this investigation was to test the maximum efficiency of the drying agent, the introduction of a large quantity of water-vapour was unnecessary, as most of the moisture was undoubtedly taken up by the first few cm. of the granular calcium chloride, so, in other experiments, air, before entering the tube, was previously passed over a long column of the fused chloride. The desiccating action of the granular salt, then, was due only to adsorption. Following are two of several experiments which were conducted with results very similar to the above. The calcium chloride tube was dried after each experiment by heating to about 275° with a current of dry air passing through it.

EXPERIMENT II.

Temperature . ..	25°					
Litres per hour ..	4·7	4·7	5·0	5·0	4·7	4·9
Litres of air.. ..	46·9	46·6	46·7	46·4	46·4	46·6
Mgrm. of residual water-vapour ..	+0·1	−0·3	+0·1	+0·1	+4·4	+7·5

Volume of air dried with maximum efficiency, 186 litres.

EXPERIMENT III.

Temperature	25°			
Litres per hour	23	24	22	24
Litres of air..	46·6	46·6	48·0	48·0
Mgrm. of residual water-vapour	−0·2	+0·3	+1·7	+5·3

Volume of air dried with maximum efficiency, 93 litres.

It may be noted from the above experiments that anhydrous chloride of calcium, in the porous state, removes at a rapid rate every weighable trace of moisture from a comparatively large volume of gas. The amount of air that may be dried with maximum efficiency decreases as the rate increases, but not in a direct proportion, for at 23 litres per hour the volume was only about half as great as at 5 litres per hour. After the period of maximum efficiency the vapour pressure of calcium chloride rises at a moderately uniform rate; however, no attempt has been made to determine how it varies with the amount of moisture adsorbed. From a comparison of Experiment I., in which the aqueous pressure of the incurrent air was 23·76 mm., with Experiments II. and III., in which the aqueous pressure was only 0·35 mm. (*loc. cit.*), it is evident that the efficiency of a calcium chloride drying tube does not depend on the quantity of water-vapour in the gas that is being dried, but rather on the volume of gas and the rate of flow.

All the samples of granular chloride of calcium that we have examined contain a small amount of surface moisture, so their efficiency lies between that of the anhydrous granular salt and the fused. The vapour pressures of several samples of Merck's "chemically pure" granular calcium chloride were determined by the method employed above, and were found to be constant for a given sample at a given temperature if no large amount of water were introduced into the tube or removed from it. In every case the vapour pressure of porous chloride of calcium was found to be less than that of the fused salt at the same temperature. For example, at 25° Baxter and Starkweather found the vapour pressure of fused calcium chloride to be 0·35 mm.; one sample of the granular showed, in six determinations, a vapour pressure between 0·23 mm. and 0·25 mm., while another sample was found to have a vapour pressure of 0·14 mm. to 0·16 mm. Thus the efficiency obtained from granular chloride of calcium as it is ordinarily used is variable and far below that which may be had from the completely anhydrous salt. When calcium chloride is employed where an efficient drying agent is required it should be previously heated, preferably in the tube in which it is to be used, to drive off surface moisture.

F. M. G. Johnson (*Journ. Am. Chem. Soc.*, 1912, xxxiv., 911) found that aluminium oxide was capable of practically perfect efficiency as a drying agent, and it is very probable that the desiccating action here, since it depends on the physical state of the oxide, is also one of adsorption rather than of hydration, as stated by Johnson.

It is a pleasure to acknowledge that this investigation was undertaken at the suggestion of Prof. J. B. Ford, of Trinity University, under whose direction some preliminary experiments were conducted.—*Journal of the American Chemical Society*, xxxix. No. 7.

ACID-RESISTING ALLOYS.*

By W. C. CARNELL.

THE development and progress of the chemical industry is vitally dependent on the development of materials out of which the plant equipment may be constructed. A process that is a success in a laboratory will be a success in the factory if conditions are duplicated. Platinum and glass are available in the laboratory, but may be prohibited in the factory. Platinum at 30.00 dols. per troy oz. was used for the manufacture of concentrating stills for sulphuric acid; platinum at 95.00 dols. per oz. cannot be considered. Glass has its place, but at best is unsafe for extensive processes.

The branch of the chemical industry that suffered most for materials out of which to construct apparatus was the mineral acids division.

For many years various metals and alloys were offered for which more or less acid-resisting properties were claimed. They had their uses, but as complete acid resisting materials they were not successful. With the advent of fused silica a decided advance was made, and it successfully replaced platinum in a number of processes.

In 1911 a basin of fused silica was tried out at the factory with which the writer was connected; so successful were the results that a 10-ton cascade concentrating plant for sulphuric acid was erected to replace a platinum outfit. The results were all that could be desired. The acid made was even better than that made in platinum. Fused silica is brittle and costly, and must be handled with as much care as glass.

In 1913 a material under the trade name of "Feralun" was tried out. This was a mixture of cast-iron and an abrasive, the abrasive being an alloy of aluminium and silicon. The surface of the iron was covered with the abrasive. The abrasive was acid-resisting, but the acid soon destroyed the iron, leaving a porous mass. However we found "Feralun" useful for nipples on acid tank cars.

Fused Silicon.—Silicon has acid-resisting properties that are all that could be desired for sulphuric acid, but it is more brittle than fused silica, and its use has not been very extensive.

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* Read before the Eighth Semi-annual Meeting, American Institute of Chemical Engineers, Cleveland, June, 1916. From the *Journal of Industrial and Engineering Chemistry*, viii., No 10

"*Ferro Chrome.*"—This alloy is made by the Electro Metallurgical Co., of Niagara Falls, and is a very promising product. Glacial acetic acid does not attack it; 56 and 28 per cent acetic acid attacked it slightly. Strong and weak nitric and sulphuric acids have practically no effect on the alloy. Hydrochloric acid attacked it readily. The experiments were carried out in a bowl 18 in. in diameter and 6 in. deep.

Silicon and Iron Alloy.—The materials thus far mentioned are valuable for specific purposes. The real dawn of acid-resisting alloy came with the use of "silicon iron" alloy. The beginning of the use of this alloy was about six years ago. The first advertisement the writer observed of this alloy was in the *Journal of the Society of Chemical Industry*, January 15, 1912. This was of a silicon iron alloy, "tantiron," put out by the Lennox Iron Foundry Co., Ltd., of London.

In May, 1912, after a year of experimenting, the first silicon iron alloy in the United States was put on the market under the name of "Duriron," by the Duriron Castings Co., of Dayton, Ohio. In 1913 the American rights for "Tantiron" were taken over by the Bethlehem Foundry and Machine Co., of South Bethlehem, Pa.

"Ironac" is another trade name for a silicon iron alloy made by the Houghton Co., Ltd., of London. While these are all alloys of iron and silicon, their composition is not the same.

Silicon iron alloy as put out under the above names is very resistant to all strengths of sulphuric acid, and apparatus made of this alloy is used in all forms of concentrating vessels and cooling devices for the concentration of sulphuric acid. By the use of the so-called "cascade basins" set in a proper furnace, full strength oil of vitriol is made from 50° Bé. acid. If all the fittings and coolers are made from this alloy the resulting oil of vitriol is practically free of iron after the plant has been in operation a few weeks. Where brimstone acid is used the resulting oil of vitriol should not contain over 0·0002 per cent iron. For sulphuric acid concentration the alloy is durable, and the breakage is very small. A plant properly handled will run for months without a shut-down. The success of the modern tower system for concentrating sulphuric acid has been due largely to the use of pipes and fittings made of this alloy.

Silicon iron alloy castings have extensively replaced stoneware parts for the manufacture of nitric acid. Early in 1916 the demand for nitric acid increased to enormous proportions; extensions to old nitric acid plants and the erections of new and larger plants was immediately demanded. The capacities of the stoneware factories of the country were soon taxed to their limit. Deliveries could not be made under six months, if at all. Had the production of nitric acid been dependent upon stoneware as it was a few years previous, the production of nitric acid would have been greatly curtailed, and the story of the World's War would probably be different.

The silicon iron alloy is resistant to nitric acid of various strengths. It can be cast into all the various forms required for nitric acid apparatus. Castings can be made as readily and as quickly as can those made of cast-iron. Here was the ideal substitute for stoneware. Necessity compelled its use, and to-day it has largely superseded stoneware for nitric acid production.

A large nitric acid plant equipped entirely with this alloy in the form of "Duriron" was in service for eight months, and the alloy showed no indications of corrosion or deterioration. There was practically no breakage. Fire destroyed the building housing the plant and most of the supports for the apparatus. The fire did not harm the castings, though they were exposed to intense heat. 80 per cent of the castings were recovered and put into service, and are in use at the present time. 90 per cent nitric acid made in a plant equipped with "Durion" castings showed an average iron content of 0·0014 per cent iron, while 36 Bé. nitric acid (52·30 per cent) showed 0·0042 per cent iron.

The silicon iron alloy was developed to resist acid. It not only resists acid, but it is resistant to erosion and to rust. Ground surfaces, representing the true alloy, are practically immune from rust. The rough casting may show some rust on exposure, but this is due to impurities in the surface caused by contact of the alloy with the moulding sand; this is a surface rust only and will not penetrate. The alloy is also heat-resisting when made of suitable design. For very high temperatures the walls must not be too thick. Castings do not distort on heating, but hold their form up to the melting-point.

The following data are given for "Duriron":—

Table I.—*Analysis (Approximate) of Duriron.*

	Per cent.	
Silicon . ..	14·00—14·50	Melting-point, 2500—2550° F.
Manganese .	0·25 – 0·35	Specific gravity, 7·00
Total carbon	0·20— 0·60	Compression strength, 70,000 lbs. per sq. in.
Phosphorus .	0·16— 0·20	Tensile strength, 25 per cent less than cast-iron
Sulphur ..	Under 0·05	

A bar of "Duriron" was compared with a bar of equal size of the best grade of chemical pottery, under equal conditions; the earthenware test bar broke so quickly that the testing machine gauge did not record any pressure. The "Duriron" bar broke under a load of 1000 lbs. By using a suspended vessel on an earthenware bar and gradually loading it with small pieces of metal and sand, a breaking test of 100 lbs. was obtained for the earthenware bar.

Tantiron.—Tantiron was first produced by Mr. Robert W. Lennox, of the Lennox Foundry Co., of London, about 1908. In 1913 the rights for the use of this alloy in the United States, Canada, and Mexico, were acquired by the Bethlehem Foundry and Machine Co., of South Bethlehem, Pa.

Table II.—*Analysis (Approximate) of Tantiron.*

	Per cent.	
Silicon	14·00—15·00	Melting-point about 2550° F.
Sulphur	0·05— 0·15	Specific gravity, 6 8
Phosphorus ..	0·05— 0·10	Tensile strength, 6 to 7 tons per sq. in.
Manganese ..	2·00— 2·50	
Carbon (graphite)	0·75— 1·25	

The alloy is not suitable for apparatus in which high internal pressures are to be used, unless it is strengthened by a protecting jacket. 40 to 50 lbs. is given as the maximum working pressure for an autoclave made of tantiron.

In general, silicon iron alloy cannot be cast in rectangular shapes or flat surfaces. The chemical engineer should collaborate with the foundryman in order to design shapes which can be produced in the foundry and still serve the purpose of the operating conditions required.

Conclusion.

While there is still opportunity for improvement and while there is much more to be desired in an acid-resisting material out of which to construct apparatus for the acid industry, yet, the silicon iron alloy or silicide of iron, as it has been called, has proven a boon to the acid industry; without it many things could not have been accomplished. It is more efficient than stoneware. At best, chemical stoneware, if made properly, should take ten to twelve weeks for its production. Castings of this alloy can be made and delivered in the same time it takes to make castings out of cast-iron. The limitation to castings made of this alloy are those of shop and foundry alone. One company has a foundry with a furnace capacity of 72 tons per day. To-day thousands of tons of castings made of this alloy are in use. It is finding its way in all branches of chemical industry. Since its introduction new chemical processes have been started which were impossible before because of lack of suitable apparatus. Silicon iron alloy is being improved upon rapidly, and the time does not seem far distant when all sorts of vessels will be made of this or a similar alloy that will give to the chemical industry the ideal non-corrosive material that may be fabricated into all the shapes peculiar to the needs of the industry.

ILSEMANNITE: HYDROUS SULPHATE OF MOLYBDENUM.

By WALDEMAR T. SCHALLER, Geological Survey, U.S.A.

A SECONDARY blue molybdenum mineral was described in 1871 and named ilsemannite; according to Dana ("System of Mineralogy," 1892, 6th ed., p. 202), it is cryptocrystalline and blue-black to black, becoming blue on exposure. The mineral is readily soluble in cold water to a deep blue solution. It has never been analysed quantitatively, and its composition has been assumed to be $MoO_2.4MoO_3$. Recent analysis of material from near Ouray, Utah, has shown that the amount of molybdenum in a lower state of oxidation is insignificant and that practically all of the molybdenum is present as MoO_3. Furthermore, the mineral is a sulphate, and is not an oxide nor a molybdate of molybdenum.

The occurrence of ilsemannite near Ouray, Utah, has been investigated from the geological side by Frank L. Hess, of the United States Geological Survey, who is preparing a report on this subject. The present paper, which is of a preliminary nature, aims to give briefly the mineralogical features of the blue molybdenum mineral, as the complete study has been unavoidably interrupted for a time.

The ilsemannite from Ouray, Utah, is disseminated through a rock, analysis of which shows that about 10 per cent of the sample is soluble in cold water. The analytical figures are given in Table I.

TABLE I.—*Analysis of Rock containing Disseminated Ilsemannite, from near Ouray, Utah.*

		Analysis.	Ratios.	Ratios after deducting melanterite.
Insoluble in water		90·50		
Soluble in water	FeO	0·99	0·014	
	MoO_3	2·37	0·017	0·017 1
	MoO_2	trace		
	SO_3	2·64	0·033	0·019 1
	H_2O (by diff.)	3·50	0·194	0·097 5
		100·00		

The water-soluble portion contains iron sulphate, and the consumption of permanganate in titrating this solution exactly equals the amount of iron (as ferrous iron) determined gravimetrically. There is present, therefore, only an undeterminable amount of molybdenum in a lower state of oxidation. Wells (quoted by F. W. Horton in "Molybdenum, its Ores and their Concentration," *U.S. Bur. Mines Bull.* 111, 1916, p. 15) found similarly that the deep blue mine water from the Lucania tunnel, Idaho Springs, Colo., although containing 7·98 grms. MoO_3 per litre, contained only an undeterminable trace of MoO_2. The colouring effect of this trace of MoO_2 seems to be very intense.

Tests made on ilsemannite from other localities show that iron sulphate is present in all specimens examined, and if therefore the figures for melanterite are deducted from the ratios given above, the remainder gives the ratio of $MoO_3:SO_3:H_2O$ as 1 : 1 : 5. It is suggested, therefore, that the formula of ilsemannite be taken as $MoO_3.SO_3\ 5H_2O$ until further quantitative analysis, on pure material, shows a difference. The analysis of the deep blue mine water from Idaho Springs, Colo., approximates closely, after deducting for other sulphates, to a ratio of 1 : 1 for $MoO_3:SO_3$, and this mine water is probably a solution of ilsemannite. A sulphate of molybdenum, $MoO_3.SO_3$, has been prepared artificially.

A specimen from Saxony showed abundant ilsemannite mixed with iron sulphate, and selected portions of the blue mineral gave a strong sulphate reaction, and showed only a small amount of iron. Another specimen from Carinthia gave a strong sulphate reaction with no ferrous iron, and only a trace of ferric iron. These two specimens were kindly loaned by Col. Washington A. Roebling, of Trenton, N.J. The ilsemannite from Cripple Creek, Colo., described by Lindgren and Ransome gives likewise a strong sulphate reaction ("Geology and Gold Deposits of the Cripple Creek District, Colorado," U.S. Geol. Survey Paper 54, 1906, p. 124). It is suggested that what is called a new molybdenum mineral by Horton (*op. cit.*, p. 15) is either a yellow sulphate of iron or yellow molybdite impregnated with a blue solution of ilsemannite, the combination of the blue and yellow producing green. Such a green coating was observed on the specimen from Cripple Creek, Colo.

The origin of ilsemannite should be studied in detail for each occurrence, but the following suggestions may be offered:—

1. Oxidation of molybdenite,—

$$MoS_2+O_9+6H_2O=MoO_3.SO_3\ 5H_2O+H_2SO_4.$$

2. Oxidation of jordisite (F. Cornu, *Zeit. Chem. Ind. Kolloide*, 1909, iv., 190), the colloidal form of molybdenite, the powdery character of jordisite allowing of more ready oxidation and alteration.

3. Decomposition of molybdates, the explanation offered for the formation of ilsemannite from wulfenite at Bleiberg, Carinthia.

4. The decomposition of a molybdenum bearing silicate, such as molybdosodalite (described by F. Zambonini, "Mineralogia Vesuviana," 1910, p. 254).

The analysis of ilsemannite from Utah shows a percentage of 2·37 MoO_3 for the sample of rock taken. Other samples showed only about half as much molybdic oxide, but the average percentage of water-soluble molybdenum contained in the rock as a whole is not known.—*Journal of the Washington Academy of Sciences*, vii., No. 13.

GLASS INDUSTRY REFRACTORIES WITH SPECIAL REFERENCE TO TANK FURNACES.

By COSMO JOHNS.

THE following remarks apply to the refractories used in tank furnaces. The comparatively low temperatures employed are favourable to long life, and there is an abundance of siliceous material available sufficiently refractory, so far as resistance to fusion is concerned. A high fusion-point is, however, only one of the factors to be considered. Fusibility depends on the character of the atmosphere to which the material is subjected while highly heated. The nature of the charge in glass tank furnaces is such that at the temperatures employed, alkaline dust or vapours are a significant constituent of the furnace gases. It is therefore not merely a question of a reducing or oxidising atmosphere, but of one charged with vapours or particles with a distinct corrosive action on acid materials. The effect would be most marked at the exit ports, where the products of combustion were being swept away at a high velocity through narrow openings, but, as the furnaces are reversible, the port blocks would each in turn be subjected to the corroding effect of the furnace gases. The obvious remedy would be to employ, in the portion of the furnace attacked, materials that would not suffer corrosion, or the rate of corrosion of which would be such that the efficient life of the furnace would not be affected. But the first requisite for the selection of materials with the required properties would be an accurate knowledge of the composition of the furnace gases and the temperature at which they are brought into contact with the ports of the furnace under discussion. This data could best be obtained by the glass-works staff, and would not present any serious difficulty at the working temperatures employed. This much might be said—that the more permeable and finely-divided the siliceous refractories employed the more rapid the rate of corrosion, and the solution will more likely be found in reducing the rate of corrosion so as to ensure a longer life than in searching for a material, probably expensive, the useful life of which was longer than that of the materials used in other parts of the furnace.

Though the comparatively low temperature employed simplifies the problem to some extent, it adds a complication where silica bricks are employed. Most, if not all, of the silica bricks of commerce contain free quartz. Now, the $\alpha \rightleftharpoons \beta$ inversion-point of quartz at 575° involves a considerable volume change, and is sharply reversible. In any furnace structure where silica bricks are used the interior face is subjected to the working temperature of the furnace, but the exterior is cooled by radiation or by conduction through the metallic supports in the shape of back-staves or plating. The exterior surface of the silica bricks is nearly always below 575°, and when that temperature is exceeded it can be deduced that the refractory lining has been so reduced in thickness that its useful life is nearly at an end. At some point along the temperature gradient the quartz will be at its critical point, and as there are always, necessarily, temperature fluctuations, it follows as a result that the quartz critical point will from time to time vary in its position in the brick, and a narrow zone—its width depending on the range of the temperature fluctuations—characterised by alternating stresses, will be formed parallel to the cool surface of the brick and co-extensive with it. This eventually will constitute a zone of weakness, and shearing will ultimately result. Such an effect was very clearly observed by the writer when experimenting with sand-lime bricks as an open hearth steel furnace lining. These Midhurst bricks were made from carefully selected and well-graded silica sand, sufficient lime being employed to form a bond of hydrous lime silicate—probably $CaSiO_3H_2O$—when subjected to high-pressure steam for some hours in an autoclave. As they were not burnt, all the silica sand remained as quartz. When carefully heated, the lime silicate became dehydrated, and the normal lime silicate found in burnt silica bricks was formed. The expansion of the heated face of the brick, due to the quartz-tridymite inversion, was considerable, and necessitated the provision of adequate expansion space. So far as refractoriness at high temperatures was concerned, the behaviour of the bricks was excellent, equal to any other silica brick tried, and superior to some. When at a later stage, during repairs, the sand-lime bricks were examined, the presence of the zone of stress, with distinct evidence of fracture along parallel lines through the silicate of lime-cement and with free quartz abundant on both sides of the zone of fracture, was evident. The presence of free quartz in silica bricks thus has evident disadvantages. The refractoriness of these "Midhurst" sand-lime bricks is, however, a welcome addition to our knowledge of the properties of the acidic refractories, though the immediate application of such knowledge might not be apparent. Had the quartz sand been heated to not less than 1300° for a period sufficiently long for the quartz-tridymite inversion to be completed before the brick was made, the difficulty caused by excessive expansion in service would be overcome. There would still, however, be the disadvantage that they could only be usefully employed where a slow rate of heating before reaching the working temperature could be ensured. There would always be a temperature interval during which dehydration was in progress and the normal anhydrous lime silicate still unformed. During this interval the cohesion of the silica grains would be much reduced and the brick liable to crumble away.—*Journal of the Society of Glass Technology*, i., No. 2.

NOTICES OF BOOKS.

A Pocket-book for Chemists. By Thomas Bayley, Assoc.A.C.Sc.I. Eighth Edition, edited by Robert Ensoll. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1917. Pp. xv+425. Price 7s 6d. net.

In the last edition of this useful work a good deal of obsolete matter has been omitted to make room for new tables which will add greatly to the value of the book. The mathematical tables are particularly full for a book of this kind, and all the usual lists of physical constants, &c., are given. In addition, the book contains sections on general, gravimetric, and volumetric analysis in which instructions are given for the analysis of a large number of products, such as sugars, alcoholic liquids, milk, &c., as well as methods of qualitative and quantitative analysis of simple substances and mixtures. The full tables given in the section on gravimetric analysis are a special feature and will save much calculation. The book is conveniently and well arranged, and will be found a reliable and useful guide in the laboratory.

Eleventh Annual Report of the Executive Committee of the British Science Guild. June, 1917. London: 199, Piccadilly. Pp. 80. Price 1s.

This report contains a considerable amount of unusually interesting matter, and it is to be hoped that it will have a wide circulation. The reports of the various sub-committees show the multifarity of the work done by the members of the Guild, and in all directions the utmost endeavours are being made to push forward urgent reforms. A full report of the meeting of the Guild at the Mansion House in April is included, and the three Addresses which were given on that occasion are highly stimulating and suggestive. Lord Sydenham dealt with the question of Reconstruction, and the Rt. Hon. H. A. L. Fisher with Science in Education and Industry, while Mr. H. G. Wells had many new and true things to say about Science in the Curricula of our Schools and Universities. Mr. Wells admitted that the lack of general interest in, and appreciation of, science is partly due to the fact that the scientific specialist is ignorant of philosophy and literature, and often finds it difficult to get into touch with the ordinary man. Mr. Wells believes that compulsory Greek is the cause of the "fundamental disease from which British organisation—English more than British—is suffering," and that we shall remain "intellectually divided and enfeebled" until we free our community and our schools from it.

The Canadian Chemical Journal. Vol. I., No. 2. Toronto, June, 1917. Price 20 c. a copy; 2 dols. a year. Published monthly by the Biggar Press, Limited.

The *Canadian Chemical Journal* has appeared at an opportune moment, and it is to be hoped that it will have a long and vigorous life, winning success and doing good. Millions are invested in the chemical industries in Canada, and an increasing number of the public are interested in scientific industries generally. It is estimated that Canada possesses 40 per cent of the water-power of the world, and the next few years should witness a great extension of chemical industries in the country, especially the electrolytic preparation of chemicals. From the articles in this copy of the new journal it may be foretold that it is going to have a useful career, and to render valuable assistance in putting a final stop to Germany's monopoly of chemicals and chemical products in the world's markets.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 24, June 11, 1917.

Ammonio-cobaltic Molybdate, Tungstate, and Vanadate. Determination and Separation of Cobalt.—Adolphe Carnot.—When ammonia and hydrogen peroxide are added to a solution of a cobaltous salt containing excess of ammonium chloride the roseo-cobaltic chloride is formed which is represented by the formula $[Co(NH_3)_5H_2O]Cl_3$. This is gradually transformed, under the action of ammonia and a moderate temperature, into purpureo-cobaltic chloride, $[Co(NH_3)_5Cl]Cl_2$, and on heating more a luteo-cobaltic chloride, $Co(NH_3)_6Cl_3$, is formed. These three chlorides, after neutralisation by an acid, give precipitates with ammonium molybdate, and the two first can be used for determining cobalt. Similar tungstates and vanadates are formed, but are not as suitable for estimating cobalt. The formation of the molybdate precipitate can be used to separate cobalt from nickel.

No. 25, June 18, 1917.

Sulphates of Zirconyl.—Ed. Chauvenet.—The author has continued his study of the mode of formation and the constitution of the six sulphates of zirconium already described. He finds that they are all derivatives of the zirconyl radical. The neutral sulphate of zirconyl, $ZrOSO_4$, exists in the anhydrous state, and also forms three hydrates with 1, 2, and 4 molecules of water respectively. The acid sulphate, $ZrOSO_4SO_3$, also exists, and two hydrates with 1 and 4 molecules of water. Four basic sulphates may be obtained:—$(ZrOSO_4)_nZrO_2$, where $n=1$, 2, 3, or 5. The first three of these form hydrates with 8, and the last with 12 molecules of water.

Action of Iodine on Alkalis.—J. Bougault.—In presence of alkalis a state of equilibrium ensues between iodine, hypoiodite, alkali, and iodide. The iodate which is formed does not appear in the equilibrium. In presence of free soda the oxidising power of iodine expressed in terms of hypoiodite decreases very rapidly after being very high at first. In a few minutes almost all the iodine has passed into the form of iodate, and the iodate may be looked upon as the result of the oxidising action of the reagent upon itself. In presence of sodium carbonate the reactions are qualitatively identical but much slower. With bicarbonate of sodium no iodate is formed, even after several days, and no hypoiodate. The latter, however, can be obtained by adding hyposulphite very slowly to a mixture of iodine and bicarbonate.

Condensation, under the Action of Potash, of Cyclohexanol with Isopropyl Alcohol. Synthesis of Cyclohexylisopropyl Alcohol.—Marcel Guerbet.—When cyclohexanol condenses with isopropyl alcohol in presence of potash the alcohol formed is cyclohexyliso-propyl alcohol, $C_6H_{11}.CH_2.CHOH.CH_3$. It yields the corresponding acetone when oxidised with chromic mixture, and this on further oxidation gives acetic and hexahydrobenzoic acids.

MISCELLANEOUS.

Historic Firms of Great Britain and Ireland.—Messrs. Fawcett and Co., of 125, Strand, London, W.C. 2, announce the preparation of a history of British commercial houses which have been established over 100 years, under the title, "Historic Firms of Great Britain and Ireland." They will be greatly obliged if firms coming under the scope of the publication will communicate with them, giving the fullest possible particulars, and stating the nature of the material available in the way of ancient prints and documents, portraits, &c., illustrative of the history of the house.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Metapara-Fraction of Cresylic Acid.—A correspondent writes:—We should be glad to know whether you could give us any information as to the possibility of purchasing in this country metapara-fraction of cresylic acid, also crystal phenol. If there is any difficulty in procuring supplies of the above at the present time, owing to war conditions prevailing, perhaps you could give us some information as to whether these chemicals are ordinarily procurable in normal times. We shall appreciate any data you can furnish on this subject.—J. and P. Hill.

TO comply with Regulation 8 (5) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

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THE CHEMICAL NEWS

VOL. CXVI., No. 3014.

THE INFLUENCE OF UNSATURATION UPON THE MOLECULAR VOLUMES OF SOLID COMPOUNDS.

By GERVAISE LE BAS.

IT has been shown from a study of the molecular volumes of the complex olefines dodecylene-octadecylene at the melting-point, that the ethenoid linkage | : | causes a contraction of—

$$\Delta = -2{\cdot}56$$

(*Phil. Mag.*, 1908, [6], xvi., 91, 66).

No other examples, drawn from open-chain compounds, can be given at present. The unsaturation of rings can, however, be studied.

Naphthalene, $C_{10}H_8$ | : | 5.

V_{17} 110·45 $(CO_2H)2H_2O$ W 25
48 × 2·584 124·03 V_{17} 78·04 V/W = 2·60
$(CO_2CH_3)_2$ W 32
5 | : | −135·8 V_{17} 82 75 V/W = 2·586
| : | −2·71

Another case drawn from the hydrocarbons is here given :—

Diphenyl, $C_{12}H_{10}$.

d 1·164 V_m 132·3
n | : | 6 W 58 58 × 2·56 148·5
6 | : | −16·2
| : | −2·70

Hexachlorethane —
$Cl_3C.CCl_3$ W 44
V_m, 117·8 Schröder, V/W 2·678

p-Dichlorbenzene—
$C_6H_4Cl_2$ m.p. 53 d_4, 1·467 (Schröder)
d, 1·459 (Jungfleisch)
V_m 100 0
40 × 2·678 107·2
3 | : | −7·2 (3 × 2·60)

Trichlorbenzene—
$C_6H_3Cl_3$ d_{10}, 1·578 (Jungfleisch)
V_m 115·3 (solid)
45 × 2·678 120·5
−5·2

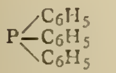
Tetrachlorbenzene—
$C_6H_2Cl_4$ m.p. 50 d_{10}, 1·7344
V_m 124·8
50 × 2·678 133·9
3 | : | −9·1
Average, −7·2 (3 × 2·60)

A number of very interesting cases are drawn from other classes of compounds.

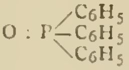
Phosphorus Compounds.

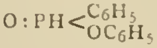
(P = 5H. H = 2 665).

n | : |. W. V_m.


$P(C_6H_5)_3$ 9 92 220·0
92 × 2 665 245·2
9 | : | −25·2
| : | −2·80

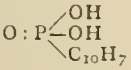
n | : W. W_m.


$O:P(C_6H_5)_3$ 9 95 229·3
95 × 2·665 253·2
9 | : | −23 9
| : | −2 66


$O:PH<^{C_6H_5}_{OC_6H_5}$ 6 69 162·7
69 × 2·665 183·9
−21·3
6 | : | −16·0

Some oxygen compounds contain augmented contractions.

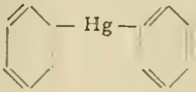
$O:PH_2.O.C_{10}H_7$ 5 59 139 6
59 × 2·577 152·0
5 | : | −12·6
| : | −2·52


$O:P(OH)_2C_{10}H_7$ 5 61 144·4 (after fusion)
61 × 2·577 157·2
5 | : | −12 8
| : | −2·56

Illustrations of the above principle may be derived from tbə organo-metallic compounds.

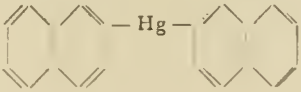
Hg 15·78 6 H H 2·626

Mercury diphenyl,—



6 64 152·3
64 × 2·626 168 06
6 | : | −15·76
| : | −2 6?

Mercury di-naphthyl,—



10 100 235 7
100 × 2·626 262 6
10 | : | −26·9
| : | −2·69

Perhaps the most interesting cases are those derived from the metallic salts of certain metallic acids, because they not only illustrate the principle already shown, but also because they furnish decisive evidence in favour of the relative volumes of the metals and other elements which may be derived from a study of solid compounds.

Silver Salts (Schröder).

Ag 10·28 (4 × 2·57).

	n| |.	W.	V_m.	W × 2 57	Δ
Silver acetate— CH_3 COAg	0	20	51·6	51·4	
Silver benzoate— C_6H_5.COOAg	3	42	101·4	107·9	−6·5 3 × 2·16
Silver cinnamate— C_6H_5 CH:CH.COOAg ..	4	52	123·0	133·6	−10 6 4 × 2 65

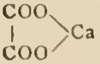
Ammonium Salts (Schiff).

NH_4 7·25.

Ammonium oxalate—					
$NH_4 O CO.CO.ONH_4.H_2O$	0	37·5	96·3	96·6	
$NH_4O.CO.CO.OH$	0	26·3	80·3	80·4	
Ammonium benzoate—					
$C_6H_5.COONH_4$	3	46	110·0	116·4	– 6 4 3×2·13

Calcium Salts (Schr).

Ca 12·85 (5×2·57).

Calcium formate—					
$(HCOO)_2Ca$	0	25	64·3	64·2	
Calcium oxalate—					
 $\begin{matrix}COO\\ \vert \\ COO\end{matrix}>Ca$	0	23	58·5	59·1	
Hydrated calcium benzoate—					
$(C_6H_5.COO)_2Ca.3H_2O$ ..	6	96	232·3	246·7	–14·4 6×2·40

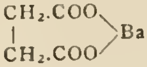
Barium Salts.

Ba 30·74 (12×2·57). Ba is usually equal to 6H.

Barium butyrate—					
$(C_3H_7.COO)_2Ba$	0	68	173·0	174·6	
Hydrated barium benzoate—					
$(C_6H_5.COO)_2Ba.3H_2$ ..	6	103	249·3	264·7	–15·4 6×2·57

Barium Salts (Schr).

Ba 6H, 8H, or 12 N.

Barium formate, Ba 8H—					
$(H.COO)_2Ba$	0	28	71·2	71·9	
Barium acetate, Ba 8H—					
$(CH_3.COO)_2Ba$	0	40	104·6	102·8	
Barium propionate, Ba 12H—					
$(C_2H_5.COO)_2Ba$	0	56	144·0	144·0	
Barium butyrate, Ba 12H—					
$(C_3H_7.COO)_2Ba$	0	68	173·0	174·6	
Barium succinate, Ba 6H—					
 $\begin{matrix}CH_2.COO\\ \vert \\ CH_2.COO\end{matrix}>Ba$	0	36	93·9	92·5	
Hydrate barium benzoate, Ba 8H—					
$(C_6H_5.COO)_2Ba.3H_2$ . ..	6	99	240·8	254·4	– 13 6 (6×2·27)

The above examples are decisive evidence in favour of the principle *that unsaturation such as is found in ethenoid linkages results in a compression of one unit.*

The case of silver cinnamate is decisive evidence that the contractions associated with the rings are similar to the contraction due to an undoubted olefin link.

The results for the salts of the organic acids show:—

(*a*) That ring structure produces no effect upon the volume.

(*b*) That the ratios—

Ag, 4H; N, 4H; Ca, 5H; Ba, 12H;

together with those for carbon and oxygen,—

$C = 4H,\ O_2 - 5H,\ >O\ 3H,$

are significant.

They can be proved to be correct from extensive study of the molecular volumes of solids. This has been accomplished by the writer, and will be published in due course.

Many of the ratios are the same as those obtained by Drude by means of the dispersion of substances, and they accord with the results of the electronic theory.

It should be remarked that it has been sought to obtain the data for a single series from the work of a single experimenter. The molecular volumes of solids are subject to unknown conditions which alter the volumes in a surprising manner. This, of course, is well known. Determinations for different substances may therefore not be comparable owing to the overlapping of these unknown conditions.

THE COMPLEXITY OF THE CHEMICAL ELEMENTS.[*]

By Prof. FREDERICK SODDY, M.A., F.R.S.

(Concluded from p. 87).

Thorium and Ionium.

A SECOND quite independent case of a difference in atomic weight between isotopes has been established. It concerns the isotopes thorium and ionium, and it is connected in an important way with the researches which, on two previous occasions, I have given an account of here, the researches on the growth of radium from uranium, which have been in progress now for fourteen years. It is the intervention of ionium and its very long period of life which has made the experimental proof of the production of radium from uranium such a long piece of work. Previously only negative results were available. One could only say, from the smallness of the expected growth of radium, that the period of average life of ionium must be at least 100,000 years, forty times longer than that of radium, and, therefore, that there must be at least forty times as much ionium by weight as radium in uranium minerals, or at least 13·6 grms. per 1000 kilos. of uranium. Since then further measurements, carried out by Miss Hitchins last year, have shown definitely for the first time a clear growth of radium from uranium in the largest preparation, containing 3 kilos. of uranium, and this growth, as theory requires, is proceeding according to the square of the time. In three years it amounted to 2×10^{-11} grms. of radium, and in six years to just four times this quantity. From this result it was concluded that the previous estimate of 100,000 years for the period of ionium, though still of the nature of a minimum rather than a maximum, was very near to the actual period.

Joachimsthal pitchblende, the Austrian source of radium, contains only an infinitesimal proportion of thorium. An ionium preparation separated, by Auer von Welsbach, from 30 tons of this mineral, since no thorium was added during the process, was an extremely concentrated ionium preparation. The atomic weight of ionium—calculated by adding to the atomic weight of its product, radium, four for the α-particle expelled in the change—is 230, whereas that of thorium, its isotope, is slightly above 232. The question was whether the ionium-thorium preparation would contain enough ionium to show the difference. Hönigschmid and Mlle. Horovitz have made a special examination of the point, first redetermining as accurately as possible the atomic weight of thorium and then that of the thorium-ionium preparation from pitchblende. They found 232·12 for the atomic weight of thorium, and by the same method 231·51 for that of the ionium-thorium. A very careful and complete examination of the spectra of the two materials showed for both absolutely the same spectrum and a complete absence of impurities.

If the atomic weight of ionium is 230, the ionium-thorium preparation must, from its atomic weight, contain 30 per cent of ionium and 70 per cent of thorium by weight. Prof. Meyer has made a comparison of the number of α-particles given per second by this preparation with that given by pure radium, and found it to be in the ratio of 1 to 200. If 30 per cent is ionium, the activity of pure ionium would be one-sixtieth of that of pure radium, its period some sixty times greater, or 150,000 years. This confirms in a very satisfactory manner our direct estimate of 100,000 years as a minimum, and incidentally raises rather an interesting question.

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[*] A Lecture delivered at the Royal Institution, May 18, 1917.

My direct estimate involves directly the period of uranium itself, and if the value accepted for this is too high, that for the ionium will be correspondingly too low. Now, last week, Prof. Joly was bringing before you, I believe, some of his exceedingly interesting work on pleochroic halos, from which he has grounds for the conclusion that the accepted period of uranium may be too long. But since I obtained, for the period of ionium, a minimum value two-thirds of that estimated by Meyer from the atomic weight, it is difficult to believe that the accepted period of uranium can have been overestimated by more than 50 per cent of the real period. The matter could be pushed to a further conclusion if it were found possible to estimate the percentage of thorium in the thorium-ionium preparation, a piece of work that ought not to be beyond the resources of radio-chemical analysis. This would then constitute a check on the period of uranium as well as on that of ionium. Such a direct check would be of considerable importance in the determination of geological ages.

The period of ionium enables us to calculate the ratio, between the weights of ionium and uranium in pitchblende, as 17·4 to 109, and the doctrine of the non-separability of isotopes leads directly to the ratio, between the thorium and uranium in the mineral, as 41·7 to 109. This quantity of thorium is, unfortunately, too small for direct estimation. Otherwise it would be possible to devise a very strict test of the degree of non-separability. As it is, the work is sufficiently convincing. Thirty tons of a mineral containing a majority of the known elements in detectable amount, in the hands of one whose researches in the most difficult field of chemical separation are world renowned, yield a preparation of the order of one-millionth of the weight of the mineral, which cannot be distinguished from pure thorium in its chemical character. Anyone could tell in the dark that it was not pure thorium, for its α-activity is 30,000 times greater than that of thorium. This is then submitted to that particular series of purification designed to give the purest possible thorium for an atomic weight determination, and it emerges without any separation of the ionium, but with a spectrum identical with that of a control specimen of thorium similarly purified. The complete absence of impurities in the spectrum show that the chemical work has been very effectively done, and the atomic weight shows that it must contain 30 per cent by weight of the isotope ionium, a result which agrees with its α-activity and the now known period of the latter.

Determination of Atomic Weights.

The results enumerated thus prove that the atomic weight can no longer be regarded as a natural constant, or the chemically pure element as a homogeneous type of matter. The latter may be, and doubtless often is, a mixture of isotopes varying in atomic weight over a small number of units, and the former then has no exact physical significance, being a mean value in which the proportions of the mixture as well as the separate atomic weights are both unknown. New ideals emerge and old ones are resuscitated by this development. There may be after all a very simple numerical relation between the true atomic weights. The view that seems most probably true at present is that while hydrogen and helium may be the ultimate constituents of matter in the Proutian sense, and the atomic weights therefore approximate multiples of that of hydrogen, small deviations, such as exist between the atomic weights of these two costituent elements themselves, may be due to the manner in which the atom is constituted, in accordance with the principle of mutual electro-magnetic mass, developed by Silberstein and others. The electro-magnetic mass of two charges in juxtaposition would not be the exact sum of the masses when the charges are separated. The atomic weight of hydrogen is 1·0078 in terms of that of helium as 3·99, and that the latter is not exactly four times the former may be the expression of this effect. Harkins and Wilson have recently gone into the question with some thoroughness, and the conclusion of most interest in the present connection, which appears to emerge, is in favour of regarding most of the effect to occur in the formation of helium from hydrogen, and very little in subsequent aggregations of the helium. In the region of the radio-elements, where we have abundant examples of the expulsion of helium atoms as α particles, it seems as if we could almost safely neglect this effect altogether. Thus radium has the atomic weight almost exactly 226, and the ultimate product almost exactly 206, showing that in 5 α and 4 β-ray changes the mean effect is nil, and the atomic weights are moreover integers in terms of oxygen as 16, or helium 4. It is true that the atomic weights of both thorium and uranium are between 0·1 and 0·2 greater than exact integers, but it is difficult to be sure that this difference is real.

When, among the light elements, we come across a clear case of large departure from the integral value, such as magnesium 24·32 and chlorine 35·46, we may reasonably suspect the elements to be a mixture of isotopes. If this is true for chlorine it suggests a most undesirable feature in the modern practice of determining atomic weights. More and more the one method has come to be relied upon: the preparation of the chloride of the element and the comparison of its weight with that of the silver necessary to combine with the chlorine, and with the weight of the silver chloride formed.

Almost the only practical method, and that a very laborious and imperfect one, which may be expected to resolve a mixture of isotopes, is by long-continued fractional gaseous diffusion, which is likely to be the more effective the lower the atomic weight. Assume, for example, chlorine were a mixture of isotopes of separate atomic weights 34 and 36, or 35 and 36. The 34 isotope would diffuse some 3 per cent faster than the 36, and the 35 some 1·5 per cent faster.

The determination of the atomic weight of chlorine in terms of that of silver has reached now such a pitch of refinement that it should be able to detect a difference in the end fractions of the atomic weight of chlorine, if chlorine or hydrogen chloride were systematically subjected to diffusion. It is extremely desirable that such a test of the homogeneity of this gas should be made in this way.

Clearly a change must come in this class of work. It is not of much use starting with stuff out of a bottle labelled "purissimum" or "garantirt." and in determining to the highest possible degree of accuracy the atomic weight of an element of unknown origin. The great pioneers in the subject, like Berzelius, were masters of the whole domain of inorganic chemistry, and knew the sources of the elements in Nature first hand. Their successors must revert to their practice and go direct to Nature for their materials, must select them carefully with due regard to what geology teaches as to their age and history, and, before carrying out a single determination, they must analyse their actual raw materials completely, and know exactly what it is they are dealing with. Much of the work on the atomic weight of lead from mixed materials is useless, for failure to do this. They must rely more on the agreement, or disagreement, of a great variety of results by methods as different and for materials as different as possible, rather than on the result of a single method pushed to the limit of refinement, for an element provisionally purified by a dealer from quite unknown materials. The preconceived notion, that the results must necessarily agree if the work is well done, must be replaced by a system of co-operation between the workers of the world checking each other's results for the same material. A year ago anyone bold enough to publish atomic weight determinations, which were not up to the modern standards of agreement among themselves, would have been regarded as having mistaken his vocation. If these wider ideals are pursued, all the labour that has been lavished in this field, and which now seems to have been so largely wasted, may possibly bear fruit, and where the newer methods fail, far below the narrow belt, of elements which it is possible to watch changing, the atomic weight worker may be able to pick up the threads of the great story. No doubt it is writ in full in the natural records preserved by rock and mineral, and the evidence of the atomic weights may be able to carry to a triumphant conclusion the course of elementary evolution, of which as yet only an isolated chapter has been deciphered.

The Structure of the Atom.

The third line of recent advance, which does much to explain the meaning of the isotopes and the Periodic Law, starts from Sir Ernest Rutherford's nuclear theory of the atom, which is an attempt to determine the nature of atomic structure, which again is the necessary preliminary to the understanding of the third aspect in which the elements are or may be complex. That uranium and thorium are built up of different isotopes of lead, helium, and electrons is now an experimental fact, since they have been proved to change into these constituents. But the questions how they are built up, and what is the nature of the non-radioactive elements, which do not undergo changes, remain unsolved.

Prof. Bragg showed in 1905 that the α-particles can traverse the atoms of matter in their path almost as though they were not there. As far as he could tell, and the statement is still true of the vast majority of α-particles colliding with the atoms of matter, the α-particle ploughs its way straight through, pursuing a practically rectilinear course, losing slightly in kinetic energy at each encounter with an atom, until its velocity is reduced to the point at which it can no longer be detected. From that time the α-particle became, as it were, a messenger that could penetrate the atom, traverse regions which hitherto had been bolted and barred from human curiosity, and on re-emerging could be questioned, as it was questioned, effectively by Rutherford, with regard to what was inside. Sir J. J. Thomson, using the electron as the messenger, had obtained valuable information as to the number of electrons in the atom, but the massive material α-particle alone can disclose the material atom. It was found that, though the vast majority of α-particles re-emerge, from their encounters with the atoms, practically in the same direction as they started, suffering only slight hither and thither scattering due to their collisions with the electrons in the atom, a minute proportion of them suffer very large and abrupt changes of direction. Some are swung round, emerging in the opposite to their original direction. The vast majority, that get through all but undeflected, have met nothing in their passage save electrons, 8000 times lighter than themselves. The few that are violently swung out of their course must have been in collision with an exceedingly massive nucleus in the atom, occupying only an insignificant fraction of its total volume. The atomic volume is the total volume swept out by systems of electrons in orbits of revolution round the nucleus, and beyond these rings or shells guarding the nucleus it is ordinarily impossible to penetrate. The nucleus is regarded by Rutherford as carrying a single concentrated positive charge, equal and opposite to that of the sum of the electrons.

Chemical phenomena deal almost certainly with the outermost system of detachable or valency electrons alone, the loss or gain of which conditions chemical combining power. Light spectra originate probably in the same region, though possibly more systems of electrons than the outermost may contribute, while the X-rays and γ rays seem to take their rise in a deep-seated ring or shell around the nucleus. But mass phenomena, all but an insignificant fraction, originate in the nucleus.

In the original electrical theory of matter, the whole mass of the atom was attributed to electrons, of which there would have been required nearly 2000 times the atomic weight in terms of hydrogen as unity. With the more definite determination of this number, and the realisation that there were only about half as many as the number representing the atomic weight, it was clear that all but an insignificant fraction of the mass of the atom was accounted for. In the nuclear hypothesis this mass is concentrated in the exceedingly minute nucleus. The electro-magnetic theory of inertia accounts for the greater mass if the positive charges that make up the nucleus are very much more concentrated than the negative charges which constitute the separate electrons. The experiments on scattering clearly indicated the existence of such a concentrated central positive charge or nucleus.

The mathematical consideration of the results of α-ray scattering, obtained for a large number of different elements, and for different velocities of α ray, gave further evidence that the number of electrons, and therefore the + charge on the nucleus, is about half the number representing the atomic weight. But van der Brock, reviving an isolated suggestion from a former paper full of suggestions on the Periodic Law, which were, I think, in every other respect at fault, suggested that closer agreement with the theory would be obtained if the number of electrons in the atom, or the nuclear charge, was the number of the place the element occupied in the Periodic Table. This is now called the atomic number, that of hydrogen being taken as 1, helium 2, lithium 3, and so on to the end of the table, uranium 92, as we now know. For the light elements it is practically half the atomic weight; for the heavy elements rather less than half.

I pointed out this accorded well with the law of radioactive change that had been established to hold over the last thirteen places in the Periodic Table. This law might be expressed as follows: The expulsion of the α-particle carrying two positive charges lowers the atomic number by two, while the expulsion of the β-particle, carrying a single negative charge, increases it by one. In ignorance of van der Broek's original suggestion, I had, in representing the generalisation, shown the last thirteen places as differing by unit by unit in the number of electrons in the atom.

Then followed Moseley's all-embracing advance, showing how from the wave-lengths of the X-rays, characteristic of the elements, this conception explained the whole Periodic Table. The square roots of the frequency of the characteristic X-rays are proportional to the atomic numbers. The total number of elements existing between uranium and hydrogen could thus be determined, and it was found to be ninety-two, only five of the places being vacant. The "exceptions" to the Periodic Law, such as argon and potassium, nickel and cobalt, tellurium and iodine, in which an element with higher atomic weight precedes instead of succeeds one with lower, was confirmed by the determination of the atomic numbers in every case. From now on this number, which represents the + charge on the nucleus, rather than the atomic weight, becomes the natural constant which determines chemical character, light and X ray spectra, and, in fact, all the properties of matter, except those that depend directly on the nucleus—mass and weight on the one hand, and radioactive properties on the other.

What, then, were the isotopes on this scheme? Obviously they were elements with the same atomic number, the same *net* charge on the nucleus, but with a differently constituted nucleus. Take the very ordinary sequence in the disintegration series, one α- and two β-rays being successively expelled in any order. Two + and two − charges have been expelled, the *net* charge of the nucleus remains the same, the chemical character and spectrum the same as that of the first parent, but the mass is reduced 4 units because a helium atom, or rather nucleus, has been expelled as an α-particle. The mass depends on the *gross* number of + charge in the nucleus, chemical properties on the difference between the gross number of + and − charges. But the radioactive properties depend not only on the gross number of charges but on the constitution of the nucleus. We can have isotopes with identity of atomic weight, as well as of chemical character, which are different in their stability and mode of breaking up. Hence we can infer that this finer degree of isotopy may also exist among the stable elements, in which case it would be completely beyond our present means to detect. But when transmutation becomes possible such a difference would be at once revealed.

The case is not one entirely of academic interest, because it is probable that the reconciliation of the conflicting views of the geologists and chemists, who concluded that lead was not the ultimate product of thorium, and those who by atomic weight demonstrations on the lead have shown that it is, depends probably on this point.

As has long been known, thorium-C, an isotope of bismuth, disintegrates dually. For 35 per cent of the atoms disintegrating, an α-ray is expelled followed by a β-ray. For the remaining 65 per cent the β-ray is first expelled and is followed by the α-ray. The two products are both isotopes of lead, and both have the same atomic weight, but they are not the same. More energy is expelled in the changes of the 65 per cent fraction than in those of the 35 per cent. Unless they are both completely stable a difference of period of change is to be anticipated.

The same thing is true for radium-C, but here all but a very minute proportion of the atoms disintegrating follow the mode followed by the 65 per cent in the case of thorium-C. The product in this case, radium-D, which, of course, is also an isotope of lead, with atomic weight 210, is *not* permanently stable, though it has a fairly long period, 24 years. The other product is not known to change further, but then, even if it did, it is in such small quantity that it is doubtful whether the change would have been detected. But, so far as is known, it forms a stable isotope of lead of atomic weight 210, formed in the proportion of only 0·03 per cent of the whole.

Now the atomic weight evidence merely shows that *one* of the two isotopes of lead formed from thorium is stable enough to accumulate over geological epochs, and it does not necessarily follow that both are. Dr. Arthur Holmes has pointed out to me that the analysis I gave of the Ceylon thorite leads to a curiously anomalous value for the age of the mineral. The quantity of thorium lead per grm. of thorium is 0·0062, and this divided by the rate at which the lead is being produced, $4\cdot72 \times 10^{-11}$ grm. of lead per grm. of thorium per year, gives the age as 131 million years. But a Ceylon pitchblende, with uranium 72·88 per cent and lead 4·65 per cent, and ratio of lead to uranium as 0·064, gives the age as 512 million yeara. Dr. Holmes regards the two minerals as likely to be of the same age, and the pitchblende to be, of all the Ceylon results, the one most trustworthy for age measurement.

If we suppose that, as in the case of radium-D, the 65 per cent isotope of lead derived from thorium is *not* stable, and that only the 35 per cent isotope accumulates, the age of the mineral would be 375 million years, which the geologists are likely to consider much more nearly the truth. But the most interesting point is, that, if we take the atomic weight of the lead isotope derived from uranium as 206·0, and that derived from thorium as 208·0, and calculate the atomic weight of the lead in Ceylon thorite, assuming it to consist entirely of uranium lead and of only the 35 per cent isotope from thorium, we get the value 207·74, which is exactly what I found from the density, and what Prof. Hönigschmid determined (207·77).

The question remains, if this is what occurs, what does this unstable lead change into? If an α particle were expelled mercury would result, or if a β-particle bismuth, two elements of which I could find no trace in the lead group separated from the whole 20 kilos. of mineral. But if an α- and a β-particle were both expelled, the product would be thallium, which is present in amount small but sufficient for chemical as well as spectroscopic characterisation. If the process of disintegration does proceed as suggested, it should be possible to trace it, for this particular lead should give a feeble specific α- or β-radiation, in addition, of course, to that due to other lead isotopes. So far it has not been possible to test this. In the meantime, the explanation offered is put forward provisionally as being consistent with all the known evidence.

Looking for a moment in conclusion at the broader aspects of the new ideas of atomic structure, it seems that though a sound basis for further development has been roughed out, almost all the detail remains to be supplied. We have got to know the nucleus, but beyond the fact that it is constituted, in heavy atoms, of nuclei of helium and electrons, nothing is known. Whilst as regards the separate shells or rings of electrons which neutralise its charge and are supposed to surround it, like the shells of an onion, we really know nothing yet at all. The original explanation, in terms of the electron, of the periodicity of properties displayed by the elements, still remains all that has been attempted. We may suppose, as we pass through the successive elements in the table, one more electron is added to the outermost ring for each unit increase in the charge on the nucleus, or atomic number, and that when a certain number, 8 in the early part of the table, 18 later, a complete new stable shell or ring forms, which no longer participates directly in the chemical activities of the atom. Thanks, however, to Moseley's work, this now is not sufficiently precise; for we know the exact number of the elements, and the various atomic numbers at which the remarkable changes, in the nature of the periodicity displayed, occur. Any real knowledge in this field will account not only for the two short initial periods, but also for the curious double periodicity later on, in which the abrupt changes of properties in the neighbourhood of the zero family alternate with the gradual changes in the neighbourhood of the VIIIth groups. The extraordinary exception to the principle of the whole scheme presented by the rare-earth elements remains a complete enigma, none the less impressive because, beyond them again in the table, the normal course is resumed and continues to the end.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

By IRVING LANGMUIR.

(Continued from p. 90).

Sublimation of Solids.—Sublimation involves two processes; evaporation and condensation. Condensation being in some ways the simpler of the two will be considered first.

Condensation of Vapours.—When a crystal is in contact with its own saturated vapour, the vapour must be continually condensing on the solid while the solid is evaporating at an equal rate. The rate at which the molecules of the vapour come into contact with the surface of the solid is given by the equation—

$$m = \sqrt{\frac{M}{2\pi RT}}\,p \quad . \quad . \quad . \quad . \quad . \quad (4),$$

where M is the molecular weight of the vapour. R is the gas constant, p is the pressure of the vapour, and m is the rate at which the gas molecules strike against the surface, expressed in grms. of vapour per sq. cm. per second. (This equation is a simple modification of the equation giving the rate of effusion of gases through small openings (Meyer's "Kinetic Theory of Gases," German edition,

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[*] From the *Journal of the American Chemical Society*, xxxviii, No. 11.

1899, 82,. Its derivation was given by the writer in an article in the *Phys. Rev.*, 1913, ii., 331. The importance of this equation in the kinetics of heterogeneous reactions can hardly be over-emphasised. See, for example, Langmuir, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1144).

When a molecule of vapour strikes against the solid surface, one of two things may happen. The molecule may be *reflected* from the surface, in other words, may rebound elastically, or it may *condense* on the surface, that is, it may be held by attractive forces in such a way that it forms at least temporarily a part of the solid body. It is of importance to know approximately what fraction of the molecules striking the surface are reflected.

In the kinetic theory of gases it has almost universally been assumed that molecules are perfectly elastic. This assumption has become so much a habit of thought that nearly everyone who has applied the kinetic theory to liquids and solids has taken it for granted that the collision between gases and surfaces of solids or liquids are also elastic. (N. T. Bacon, *Journ. Phys. Chem.*, 1913, xvii., 762, suggests that molecules are not elastic, and in this way explains qualitatively the phenomena of adsorption and catalytic action).

We have seen, however, from a consideration of the heat conductivity of solids that the time of relaxation of the atoms is usually small compared to the time necessary for the atom to complete a single oscillation. This means that before an atom can be displaced a perceptible distance the energy causing the displacement has been dissipated among all the adjacent atoms. From this fact it appears that the collisions of molecules against solid bodies must in general be almost wholly inelastic.

In a recent paper in the *Physical Review* (1916, viii., 149), the writer has discussed this question very fully, and gives abundant evidence, both experimental and theoretical, for the inelasticity of the collisions between gas molecules and solid surfaces. There are, apparently, some cases in which a moderate amount of real reflection does occur, but these cases must be looked upon as the exception rather than the rule.

According to this viewpoint the mechanism of the condensation of a vapour on a solid is as follows:—

In the vapour surrounding the solid, the average distance which the molecules travel between collisions (the mean free path) is of the order of magnitude of 10^{-5} cm. if the pressure is atmospheric, while it is correspondingly greater if the pressure is less. When a vapour molecule approaching the surface comes within a distance of about 2×10^{-8} cm. of the surface layer of atoms it begins to be acted upon by the electromagnetic field close to the surface. The vapour molecule thus experiences a force attracting it towards the surface. As it moves closer to the surface the attractive force rapidly increases and soon reaches a maximum intensity. The attractive force then rapidly decreases, and falls to zero when the molecule has travelled a distance only about $0{\cdot}6 \times 10^{-8}$ cm. beyond the point at which the force was a maximum. The point at which the force falls to zero may be regarded as an equilibrium position. When the molecule reaches this position its kinetic energy will be very high, for a relatively large amount of work has been done upon it by the attractive forces. It will therefore not remain in the equilibrium position, but will move still closer to the atoms of the solid, and will thus enter a region in which it is subjected to very strong and rapidly increasing repulsive forces. If the molecule had lost no energy to adjacent atoms it would probably travel a distance $0{\cdot}2\text{-}0{\cdot}3 \times 10^{-8}$ cm. against these repulsive forces before being brought to rest. It would then pass again through the equilibrium position, and finally out through the region of attractive forces, and might thus again escape from the surface forces, in other words, be reflected.

But the improbability of such a reflection is evident when we consider the ease with which energy is dissipated to adjacent atoms. This energy loss occurs in two ways. In the first place, when the molecule is approaching the surface, the attractive force is exerted by *several atoms* on the surface. These atoms are thus all accelerated towards the incident molecule. A little later, when the molecule is in the region of repulsive forces, these forces will be exerted principally by a *single atom* of the solid. The energy used in accelerating the surface atoms can therefore only partially be delivered back to the incident molecule. This dissipation in energy, even if only relatively small, will usually make it impossible for the molecule to pass out through the region of attractive forces.

The second kind of loss of energy, which is probably the more important, is that which causes the remarkably small time of relaxation in solid bodies. We have seen that in the interior of crystals the time taken for adjacent atoms to reach thermal equilibrium with each other is of the order of 10^{-16} seconds. The duration of a collision between a molecule and a surface (that is, the time between successive passages through the region of maximum attractive force) must be of the order of 10^{-13} seconds. Thus, in general, the energy delivered to the incident molecule by the attractive forces is practically wholly dissipated to the adjacent atoms by the time the molecule first reaches the equilibrium position. It therefore has not sufficient kinetic energy to enable it to penetrate far into the region of repulsive forces, and certainly not sufficient to allow it to work against the attractive forces and thus escape from the surface.

The condensation of a vapour on a solid surface thus takes place independently of the temperature of the surface. (It must, of course, be remembered that what we ordinarily observe during the condensation of a vapour is the difference between the rate of condensation and the rate of evaporation).

This is especially evident when we consider that the intensity of the field of force close to the surface, as measured by the total surface energy γ_0, is itself independent of the temperature. The rate of evaporation, on the other hand, varies extremely rapidly with the temperature.

If practically every molecule of vapour which strikes against the surface of the solid condenses, it is not at first evident how the molecules, especially if they are complex, are able to arrange themselves to form a crystalline mass. In analysing the mechanism of condensation we must distinguish two extreme sets of conditions that may occur. These may be termed *irreversible* and *reversible* sublimation.

By *irreversible* sublimation I mean the type which occurs, for instance, when a tungsten filament is heated to a high temperature in a well evacuated bulb. Under these conditions, there can be no equilibrium, for the bulb is at a temperature thousands of degrees lower than that at which the vapour can be produced. The vapour is thus enormously superheated with respect to the surface on which it condenses. Such conditions as this can only be realised in practice when the vapour is at very low pressure, for, otherwise, the amount of vapour condensed per unit area per second would be so great that the heat liberated by the condensation could not be removed rapidly enough to maintain a low temperature on the condensing surface.

By the term *reversible* sublimation we may designate that which takes place, for example, when iodine or naphthalene is sublimed slowly at ordinary temperatures.

In this case we are dealing with small differences of temperature, and we shall see that under these conditions condensation and evaporation are going on simultaneously at nearly equal rates over every portion of the surface where condensation occurs.

The mechanisms of reversible and irreversible sublimation are in some ways quite different, and from the experimental side the phenomena show marked distinctions.

In the irreversible sublimation the vapour molecules remain where they first strike the surface, since they can neither be reflected nor re-evaporated. The deposit formed by the condensed vapour is therefore homogeneous (when gaseous impurities are absent) and is of uniform thickness, If the temperature of the surface on which condensation occurs is sufficiently low, the deposit will be wholly non-crystalline, since the atoms or molecules become rigidly fixed in position when they strike the surface and thus have no opportunity to arrange themselves as in a crystal. With the condensing surface at higher temperatures, however, a sintering or crystallising process may go on within the deposit even when the temperature is below that at which perceptible vaporisation occurs.

By means of this irreversible sublimation it is possible to obtain any volatile body in a non-crystalline form.

In the case of reversible sublimation the deposit formed from the condensed vapour is ordinarily very crystalline, frequently consisting of groups of separate crystals. In the formation of these crystals every molecule of vapour which strikes the surface condenses just as in the case of irreversible condensation, but most of these molecules re-evaporate again. The tendency of different molecules to re-evaporate will depend entirely on how firmly they are held by the atoms of the crystal. Thus the molecules which strike the surface in such a way as to form a continuation of the space lattice already present, will evaporate much less frequently than molecules which are not in positions where they can fit in with the crystal structure. The continual evaporation and condensation going on over the whole surface of the crystal allows the atoms to arrange themselves in the most stable positions. The smaller the differences in temperature and the more nearly equal the rates of condensation and evaporation, the more perfect will be the development of the crystals.

Evaporation of Solids.—We have seen that the condensation of vapours on a solid body takes place at a rate which is practically independent of the temperature. The rate of evaporation, however, increases rapidly with temperature.

Since evaporation and condensation are in general thermodynamically reversible phenomena, *the mechanism of evaporation must be the exact reverse of that of condensation*, even down to the smallest detail.

In the condensation of a monatomic vapour such as that of a metal, each atom as it approaches the surface comes into a region in which it is attracted. It is thus accelerated, but it gives up its newly acquired energy to adjacent atoms nearly as fast as it receives it. It soon reaches a region of repulsive forces, and is then brought to a stop. It then continues to move about an equilibrium position with an irregular motion due to thermal agitation.

Conversely in the evaporation of an atom of a metal the atom must acquire energy from adjacent ones and thus be accelerated outward. As it moves it must receive successive increments of energy from its neighbours until finally it passes out of the region of attractive forces. From the smallness of the time of relaxation we are thus compelled to believe that an atom only escapes when it thus receives a very large number of successive impulses from the adjacent atoms.

The very small probability of such a sequence of favourable impulses is the reason that so few atoms evaporate at lower temperatures.

We may picture to ourselves the mechanism of evaporation by imagining a large number of heavy balls suspended (according to a two dimensianal lattice) from a ceiling by steel springs. Each ball is to be coupled to each of its neighbours by springs under tension. If some of the balls are set in motion the energy will be rapidly propagated to the others so they will all be in a state of agitation. To properly imitate the structure of a solid the coupling between the balls should be so stiff that the total energy of one ball can be transmitted to its neighbours in a very small fraction of the time required for a single oscillation.

When all the balls have been in motion long enough for a steady state to have been reached, the velocities will be distributed among them according to the probability laws, in other words, according to Maxwell's distribution law.

If the springs are of brittle wire so that they snap when elongated more than a certain amount, then from time to time balls which have acquired an unusually large downward displacement will break their springs and escape. This will be quite analogous to evaporation.

The rate of evaporation of a solid is thus determined by the number of surface atoms per second which reach a certain critical condition. By means of Maxwell's distribution law it can thus be readily shown (see Note) that the rate of evaporation should increase with the temperature according to an equation of the form—

$$m = A\sqrt{T}\,\epsilon \qquad \ldots\ldots \quad (5)$$

where λ is the internal latent heat of evaporation per grm.-atom, and A is a constant whose value will depend primarily on the degree of coupling between adjacent atoms.

(Note.—Richardson, *Phil. Soc.*, 1903, cci., 516, calculated in this way the rate of evaporation of electrons from heated metals (thermionic emission). The derivation of equation 5 is also given by the writer (*Journ. Am. Chem. Soc.*, 1913, xxxv., 122), in connection with a study of the reaction between oxygen and tungsten at high temperatures. It was also pointed out that this equation is substantially equivalent to Arrhenius' equation for the temperature coefficient of reaction velocity. The significance of Maxwell's distribution law in relation to the kinetics of chemical reactions has been very fully treated in a recent paper by R. Marcellin, *Annales de Physique*, 1915, iii., 185).

In the study of the disintegration of radioactive substances, it has been customary to speak of the life or period of the atom. In a similar way we may calculate the "life" of an atom on the surface of an evaporating solid.

The number of atoms evaporating per second per sq. cm. of surface will be Nm/M where N is the Avogadro constant and M is the atomic weight of the substance. If N_0 is the total number of atoms per sq. cm. of surface, then t, the average life of an atom on the surface will be—

$$t = \frac{N_0 M}{Nm} \qquad \ldots\ldots\ldots \quad (6).$$

The "half period," that is, the time which must elapse before half of any selected lot of atoms will have evaporated, is equal to—

$$t_{1/2} = 0{\cdot}693\,\frac{N_0 M}{Nm} \qquad \ldots\ldots \quad (7).$$

We have just seen that the constant A in equation 5 is dependent on the coupling between the atoms. The time of relaxation of the atoms is also a measure of this coupling. It should thus be possible to estimate the time of relaxation from the rate of evaporation, and it will be of interest to see how the result calculated in this way compares with that found from the heat conductivity.

We see from equation 5 that the rate of evaporation, m, depends on the latent heat of evaporation. If we substitute $\lambda = 0$ in equation 5 we obtain a hypothetical value of m_0 (let this be m), that represents the rate of evaporation which would occur if attractive forces did not prevent the escape of atoms from the surface. Thus we obtain from (5)—

$$\frac{m}{m_0} = \epsilon^{-\lambda/RT} \qquad \ldots\ldots\ldots \quad (8).$$

By equation 6 the average life of an atom on the surface of a solid evaporating at the rate m_0, is—

$$t_0 = \frac{N_0 M}{N m_0} \qquad \ldots\ldots\ldots \quad (9).$$

Eliminate m_0 between (8) and (9)—

$$t_0 = \frac{N_0 M}{Nm}\,\epsilon^{-\lambda/RT} \qquad \ldots\ldots \quad (10).$$

Or from (5)—

$$t_0 = \frac{N_0 M}{NA\sqrt{T}} \qquad \ldots\ldots\ldots \quad (11).$$

The quantity t_0 thus represents the average length of time an atom would remain on the surface if there were no attractive forces to hold it. Now the "time of relaxation" has been defined as the time required for an atom to give up all but $1/e^{th}$ of its excess energy to adjacent atoms. It is evident that the time required for an atom at rest to be set in motion will also be measured by the time of relaxation. Thus t_0 should be of the same order of magnitude as the time of relaxation, and probably only differs from it by some constant factor not very far from unity.

The rates of evaporation of tungsten (*Phys. Rev.*, 1913, ii., 329), platinum, and molybdenum (*Ibid.*, 1914, iv., 377) in a very high vacuum have been measured by Mr. G. M. J. Mackay and the writer. The values of t_0, calculated from these data by equation 10 are given in Table II.

TABLE II.

	W.	Mo.	Pt.
N_0	$1{\cdot}46 \times 10^{15}$	$1{\cdot}32 \times 10^{15}$	$1{\cdot}51 \times 10^{15}$
t_0 at 300° K	$3{\cdot}4 \times 10^{-19}$	$3{\cdot}5 \times 10^{-20}$	$1{\cdot}1 \times 10^{-16}$
t_0 at 2000° K	$5{\cdot}2 \times 10^{-18}$	$1{\cdot}0 \times 10^{-18}$	$3{\cdot}0 \times 10^{-15}$
t_r by Eq. 1	$1{\cdot}3 \times 10^{-15}$	—	$2{\cdot}3 \times 10^{-15}$

For comparison, the "times of relaxation" t_r calculated by equation 1, are given in the last line. It will be remembered that equation 1 gives too high a value for t_r because it was assumed in its derivation that an atom could take up energy only from atoms in one given direction. It is seen that the order of magnitude of t_0 is not very different from that of t_r. We must not expect any very good agreement between t_0 and t_r because of the very great effect of slight errors in λ on the value of t_0 calculated by equation 10. Thus, if λ is taken 1 per cent too large, the value of t_0 will be 20 times too small. On the whole, therefore, we may conclude that the values of t_0 calculated as above, furnish confirmatory evidence that the time of relaxation of the atoms in solids is hundreds, if not thousands, of times smaller than the "natural period" of atomic vibrations.

(To be continued).

COUMARONE RESIN AND ITS USES.

By CARLETON ELLIS and LOUIS RABINOVITZ.

RESINOUS bodies obtained by the polymerising action of sulphuric acid on indene (C_9H_8) and coumarone (C_8H_6O) occurring in the fraction of coal-tar naphtha boiling between 160 and 180° C., are found in the market under the name of coumarone resin. Various attempts have been made, with some measure of success, to substitute these polymerisation products for certain of the natural resins. This paper aims to give a brief review of the subject and a résumé of some experimental work carried out by us on coumarone resin.

Coumarone (or cumarone) resin was obtained by Kraemer and Spilker, during their investigation on indene and coumarone in coal-tar naphtha (*Ber.*, 1890, xxiii., 78, 3276), by the action of strong acids, particularly sulphuric, on coumarone; they called the product *para coumarone*. Somewhat later (*Ber.*, 1900, xxxiii., 2257) they subjected this resin to a more thorough investigation and found that when pure coumarone which has been diluted with benzol is treated with a moderate amount of sulphuric acid, the greater part of the coumarone is converted into a resin soluble in benzol, while a lesser portion is transformed into a body insoluble in benzol and is carried down by the sulphuric acid, from which it may be removed by treatment with water.

The investigations of these chemists show that polymerisation begins with an acid strength of 80 per cent (monohydrate). With this strength of acid the soluble resin is obtained almost exclusively. As the concentration of the acid is increased more and more of the insoluble resin forms. Increase in the proportion of the acid acts in a similar manner. With acid of 95 per cent strength applied in sufficient amount to a 2 per cent solution of coumarone in benzol the insoluble resin is formed almost quantitatively. When using 50 per cent of acid, calculated on the coumarone taken, about 25 per cent of soluble resin is formed, while with four times the amount of acid no insoluble resin is formed.

Indene behaved very much like coumarone, only in that case the resinification was accompanied by a rise in temperature. The coumarone resin was found to melt between 107 and 108° C.

By the treatment of coumarone with a relatively large proportion of sulphuric acid (*Ber.*, 1890, xxiii., 81), at first a soft pasty mass was obtained which soon hardened to a brittle and infusible body, insoluble in all solvents. Kraemer and Spilker were unable to state whether this body corresponded in composition to that of coumarone. It had a specific gravity of 1·25 at 19° C. Its molecular weight was four times that of coumarone and on heating the resin decomposed between 300 and 350° C.

Indene was found to give a resin similar to that obtained in the case of coumarone and the product was obtained by them in various modifications, of differing melting points and molecular weights. From pure indene they obtained a resin which melted at 210° C. By treating the purified fractions that came over at 155-158° C. with sulphuric acid and steam distilling the solvents, they obtained a crude indene resin which was in many respects very similar to the coumarone resin (*Ber.*, 1900, xxxiii., 2257).

Later Kraemer and Spilker analysed the insoluble and infusible modification of coumarone resin and found that sulphur which they previously had noted and had regarded as a mere impurity was in fact chemically combined (*Ber.*, 1901, xxxiv., 1888).

In 1890 Kraemer and Spilker (*Ber.*, 1890, xxiii., 81) called attention to the industrial possibilities of "para coumarone" or "coumarone resin." They noted that it formed a coating for wood and metal surfaces which on account of its resistance to acids and alkalis possessed certain advantages over the ordinary resin solutions and varnish coatings employed for this purpose.

Wendriner, who has done a considerable amount of work on coumarone resin, describes a process for the manufacture of a light coloured resin, as well as a white solvent naphtha, from coal-tar naphtha distilling at 160-180° C., by removing first the acidic and basic constituents of the oil with 3 to 5 per cent by volume of 60° Bé. sulphuric acid under constant agitation and then treating the naphtha with 0·25 to 0·4 per cent by volume of concentrated sulphuric acid in a thin stream until the temperature rises to 110-120° C. After this treatment the acid is removed from the oil and the latter containing the dissolved resin is neutralised, dried, and distilled from the resin with superheated steam. A less pure coumarone resin is prepared by treating solvent naphtha in the presence of its acidic and basic impurities with 0·5 per cent instead of 0·25 by volume of concentrated sulphuric acid (German Patents 270,993 and 281,432; *Journ. Soc. Chem. Ind.*, 1914, 474; *Chem. Abs.*, 1914, 2248; 1915, 2001; *Z. Angew. Chem.*, xxvii., 2582). Wendriner modified the process by omitting the use of 60° Bé. acid and carrying out the polymerisation under cooling and under slow introduction of concentrated acid. He mentions that care should be taken to use an amount of concentrated acid equal to 0·25 to 0·4 per cent by volume of the naphtha treated and that the temperature should not rise above 40-50° C. The advantages of this process are: A saving of 3 to 5 per cent 60 Bé. sulphuric acid; avoidance of the danger caused by heating of the volatile naphtha; a product in appearance somewhat resembling a light Congo resin melting between 80-100° and having a colour varying from yellow to amber, depending on the care exercised in carrying out the reaction. According to Wendriner it is important to avoid sulphonation which has an influence on the colour and boiling point of the naphtha yielded by the operation.

Knüppel (German Patent 253,437, 1912; *Z. Angew.*

Chem., 1912, xxv., 2506) states that a hard brittle resin is obtained by blowing air through para coumarone and para indene for three to five hours at a more or less high temperature. According to Knüppel, the product is not tacky, dries with a high lustre, and increases the drying power of the varnish prepared from it.

Fehringer (*Chem. Abs.*, 1915, 3369; U.S. Patent 1,157,768, October 26, 1915) prepares a bronzing liquid or bronze powder varnish by dissolving coumarone resin in benzine, gasoline, benzol, chlorethylene, or a mixture of these solvents.

Varnishes are prepared from cellulose esters by dissolving them in methyl alcohol, acetone oils, ketones or the like, with the addition of polymerisation products of coumarone or indene, dissolved in benzol, alcohol, or like solvents (*Chem. Abs.*, 1915, 1850; German Patent 281,265, 1913). The resulting varnish is stated to be oily, lustrous, to dry uniformly, forming a very elastic coating which is stable in air and light. For instance, 1 part by weight of coumarone resin is dissolved in 5 parts benzol and added to a liquid consisting of a solution of 3 parts of collodion and 0·5 part of acetone oil, 10 parts each of alcohol and ketones; the resulting composition is diluted with 30 parts alcohol, 30 parts benzine, and 10 parts methyl alcohol. Or, 1 part of coumarone resin is dissolved in a mixture of 2·5 parts each of fusel oil and tetrachlorethane; this solution is added to a mixture of 60 parts acetone and 30 parts methyl alcohol: 40 parts of acetyl cellulose are dissolved in this liquid. (See also U.S. Patent 1,185,514, May 30, 1916, to Lehmann and Stocker).

Eichler (U.S. Patent 1,133,432, March 30, 1915) describes the simple preparation from the polymerisation products of coumarone of a primer and varnish which is impervious to water vapours, caustic alkalis, ammonia, and efflorescence. For example, para coumarone is melted and compounded with a solvent while heat is applied, whereupon the varnish is formed. The consistency of the varnish of course depends upon the quantity of solvent employed. Usually equal parts by weight of the resin and solvent are used. The primer and varnish may also be added to ordinary varnish to render the latter more impervious to water and more resistant to alkali. Benzine, gasoline, benzol, or turpentine are good solvents for the resin. Eichler (U.S. Patent 1,133,433, March 30, 1915) also refers to the application of coumarone resin in linseed-oil varnishes in lieu of ordinary varnish resins.

Lender and Koch (U.S. Patent 1,019,666, March 5, 1912) note that coumarone resin may be used in a varnish base for the manufacture of varnishes, enamels, and paints, and as a binder in the manufacture of linoleum, lincrusta, and oil cloth. They state that all objections encountered in the preparation of paints or varnishes by incorporating Chinese wood oil with ordinary resins are overcome, if in place of these the polymerisation products of coumarone and indene, namely, para coumarone and para indene, are employed. A varnish of this type is prepared as follows:—10 kg. of Chinese wood oil are heated to 220-240° C. and a quantity of the polymerisation products of coumarone and indene to suit the conditions of use, generally an equal weight, is added; the product is a homogeneous mass which is hard when cold. This material is the base from which varnish, lac, enamel, or similar coating material are made. This base is then heated and mixed with a suitable solvent such as liquid hydrocarbons, *e.g.* benzine, benzol, ligroin, turpentine, &c., and also chlorinated hydrocarbons. The amount of solvent used is dependent upon the consistency of the product desired and the use to be made of it. It may be thinned at will. To the mixture of the base and solvent may be added any desired colouring matter, and the varnish or paint is stated to dry rapidly to a brilliant elastic coating impervious to liquids and unattacked by gases. It is unusually resistant to water, acids, heat, and cold. A varnish paint or other similar product of this character is claimed to have a wider range of use than any other similar product or any product consisting of Chinese wood oil and ordinary resins, especially as it does not become tacky and does not set or liver by the addition of such pigments as lead or zinc compounds.

Lender (German Patent 277,605; *Z. Angew. Chem.*, 1914, xxvii., II., 583) states that a varnish can be prepared from indene or coumarone, or both, with or without the addition of vegetable or animal oil, by heating with sulphur or sulphur chloride under pressure or at ordinary pressure, and dissolving the product in a volatile solvent.

Properties of Coumarone Resin.

Bottler (*Kunststoffe*, 1915, 277), who has investigated the properties of commercial coumarone resin, states that the resin of commerce varies widely in character. Some varieties which he examined were solid and more or less brittle, others were soft and pasty. A rough and ready method for the determination of the hardness of a resin according to Bottler is to scratch the surface of the resin with a needle. On soft resins the needle traces a smooth and even line. On hard resins the line is rugged and rough.

Some of the coumarone resins, Bottler notes, were of a dark brown colour, sometimes even black, while others varied from a yellow-brown to a brown colour. They occurred in lustrous non-transparent lumps having a shiny fracture. Some of the samples gave a light yellow, others a dark brown powder. They possessed a tar-like odour. The yellow and brown resins in powder form attracted moisture from the air on standing over night. In some cases it was found necessary to use a spatula to remove the powdered material from the mortar. Their melting point varied over a considerable range. Some of the yellow-brown and brown varieties melted at 55, 60, and 65° C. The darker varieties generally melted higher, softening at about 85° C. and melting completely at 98, 100, and 108° C. They fused more easily than various natural resins. The fused material usually solidified very quickly to a resin of the original colour.

A sample of brown coumarone resin, made in this country, was examined in this laboratory and found to melt completely at 65° C.

Action of Alkalis.

A 5 per cent sodium carbonate solution, a 1 and a 5 per cent solution of sodium hydroxide, and 10 per cent ammonia water did not affect coumarone resin. Only on prolonged warming with 5 per cent caustic was the resin somewhat acted upon, and the solution shows signs of frothing. At any rate no saponification took place.

Kraemer and Spilker state that para coumarone is easily soluble in ether, benzol, and chloroform, but difficultly soluble in benzol (*Ber.*, 1890, xxiii., 81). The films obtained from different varieties of resin in either carbon tetrachloride, trichlorethylene, benzine, and turpentine possessed a certain degree of elasticity. It is stated that the resin possesses drying properties when exposed to air in thin layers (*Seifen.-Ztg.*, 1913, 289, 344, 694).

Preparation of Pure Indene.

Kraemer and Spilker (*Ber.*, 1890, xxiii., 3276) describe a process for the purification of indene by means of picric acid. According to this method the fractions of crude naphtha boiling between 176-182° C. are treated with as much picric acid as is necessary to combine with all the unsaturated bodies present. The crystalline precipitate formed contained the picrates of coumarone and naphthalene as well as that of indene. On steam distillation the indene picrate is decomposed and indene distils over. Ten kg. of crude naphtha boiling between 176-182° gave 3 kg. of crude indene. The process is not without danger as these picrates are highly explosive.

Weisberger (*Ber.*, 1909, xlii., 569, and German Pat. 205,465, 1908, and 209,694, 1909) describes several methods of a more practical nature for the preparation of pure indene. Sodium amide is treated with the crude indene fraction boiling between 175-185° C. Ammonia is evolved and

SOLUBILITIES OF COUMARONE RESINS, &C.

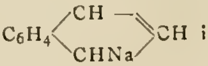
Hard Coumarone Resin (Bottler).

Solvent.		Colour of solution
Alcohol	Slightly soluble	Light yellow.
Absolute alcohol	Easily soluble	Yellow.
Carbon tetrachloride	Completely soluble	Yellow to brown.
Trichlorethylene	Completely soluble	Yellow.
Benzine	Completely soluble	Yellow to red-brown.
Turpentine	Soluble (slight residue)	Yellow.
Linseed oil	Slightly soluble	—

Soft Coumarone Resin (Bottler).

Ether	Soluble	Yellow.
Carbon tetrachloride	Completely soluble	Brownish yellow.
Trichlorethylene	Completely soluble	Brown colour.
Benxine	Easily soluble	Brownish colour.
Turpentine	Almost completely soluble	Yellowish brown colour.
Ether and 90 per cent alcohol	The resin is precipitated	—

	Colour of film on tin plate (Bottler).
Ether	Lustrous and yellow.
Carbon tetrachloride and trichlorethylene	Light yellow or yellow.
Benzine	Brownish red.
Turpentine	Yellow and lustrous.
Ether and trichlorethylene	Yellow.

amide is converted into a dark heavy oil. The mixture is heated for two hours under agitation at 110-175° C. It is then distilled at 20-30 mm. pressure to remove the unchanged hydrocarbons which come over at 110-130° C. The solid amorphous mass left behind and to which Weisberger assigned the formula  $C_6H_4\langle{}^{CH\,-}_{CHNa}\rangle CH$ is decomposed by water into indene and sodium hydroxide. The indene is recovered by steam distillation. A rough fractionation of this product yields pure indene.

A still purer product may be prepared by treating the crude indene with the theoretical quantity of metallic sodium and passing a slow stream of ammonia into the mixture at 120-130° C. for five or six hours. The indene sodium compound obtained by this process resembles rosin in appearance, is very sensitive to the action of air, and is easily decomposed by water, yielding a very pure indene.

By heating the indene and sodium above 130° C. in the presence of small amounts (2 per cent) of basic bodies such as aniline, toluidine, or pyridine, pure indene may be obtained without the use of ammonia gas. Weisberger states that by this method the yields of indene obtained from the fraction of heavy benzol boiling between 175-185° C. amounted to 35 per cent.

The methods for preparing pure coumarone are more involved and are of scientific rather than of practical interest.

The Properties of Indene and Coumarone.

Spilker and Dombrowsky (*Ber.*, 1909, xlii., 573) describe indene prepared from the sodium compound as melting at 92° C., and boiling at 182° C., having a specific gravity of 1·0002. Pure indene absorbs oxygen and becomes acid. The oxidised indene is insoluble in alcohol and cannot be distilled by steam (Weger and Billman, *Ber.*, 1903, xxxvi., 640). It combines with mercuric sulphate, giving an indene mercuric oxide compound (*Pharm.-Ztg.*, 1915, 46).

Bizzarri (*Journ. Chem. Soc.* [*Abs.*], 1891, 566) describes coumarone as a colourless liquid boiling at 169° C. and very resistive towards chemical agents or heat. Aniline or alcoholic ammonia has no action on it. Aluminium chloride was found by Heusler (*Z. Angew. Chem.*, 1869, 319) to act violently on coumarone and indene with the production of a resin soluble in hydrocarbons. He states that it is impossible by a single treatment with sulphuric acid to remove completely the indene and coumarone from coal-tar naphtha; but that by the action of aluminium chloride these two bodies may be completely resinified. Two and one-half per cent of aluminium chloride is sufficient for this purpose. The indene and coumarone resins remain dissolved in the naphtha.

Experimental Work.

In some some experimental work carried out by us, the fraction of varnish makers' solvent naphtha which boiled between 160-180° C. was treated with 1 per cent of 66° Bé. sulphuric acid and was stirred for several hours at room temperature. The temperature of the mixture did not rise above 35° C. The product was then washed free from acid and steam-distilled with superheated steam. There was left in the vessel a pasty material which gave on drying on the steam bath a transparent brown substance of the consistency of molasses. Six hours of steam distillation with superheated steam did not materially affect the hardness of this product. Some of this soft resin was heated for 15 to 20 minutes to 220° C. with about 10 per cent of sulphuric acid (66° Bé.). The resin darkened considerably and carbonised without undergoing any change in hardness. Another portion was subjected to the action of anhydrous zinc chloride and also to stannic chloride at 200° C. without undergoing any change. Chlorine combined readily with the coumarone resin, giving a fairly hard, dark product. Darkening was the only visible effect that a powerful ultravoilet light had on coumarone resin after a three-hour exposure.

The effect of other polymerising agents on solvent naphtha containing coumarone and indene was investigated in this laboratory. In one case, the naphtha was heated to boiling with reflux condenser for one hour with silver oxide. A part of the silver oxide was reduced to metallic silver with the formation of a bright mirror on the walls of the vessel. The liquid was filtered and steam-distilled. A dark brown material was left in the vessel which was considerably harder than the resin obtained with sulphuric acid. Phosphorus trichloride, phosphoric acid, chromic acid, hydrochloric acid, ammonium dichromate, formaldehyde, and potassium hydroxide did not polymerise coumarone or indene in solvent naphtha, under the conditions tried. Zinc chloride at the boiling point of solvent naphtha gave rise to a small amount of resin. The action of anhydrous stannic chloride was similar to that of zinc chloride, while iodine was without effect.

Soft coumarone resin was distilled at 29 in. vacuum.

When the temperature rose to 160° C. the distillation was stopped. The resin left in the flask was rather dark and melted completely at 60-65° C. It softened in the hands to a flexible mass which was not tacky.

Twenty grms. of the soft coumarone resin were distilled at 29 in. vacuum.

Weight of distillate (grms.).	Weight of residue (grms.).	Temperature (° C.).
9·0	10·5	to 168
2·5	8·5	168-180

From this data it can be seen that 57·5 per cent of the soft resin went over into the distillate. The hardness and melting point of the residue of resin increased with the amount of material distilled. The distillate was a highly viscous liquid which was somewhat brown in colour. This coloration was due to the small amounts of resin that were carried over mechanically during the distillation. The distillate is probably an intermediate polymerisation product. Its iodine number was found to be 28·5.

The resin obtained in this way became plastic at 38° C. and melted completely at 71° C. Its saponification number did not exceed 0·2. The iodine number of the hard resin was 38 to 43·5, which, it will be noted, is higher than the iodine number of the distillate.

In another case a sample of crude solvent naphtha, 25 per cent of which boiled above 160° C., was treated with 1 per cent of sulphuric acid of 98 per cent strength and the mixture was agitated for two hours. It was then freed from acid and distilled under ordinary atmospheric pressure at 190° C. The residue from this distillation was distilled to 165° C. under a vacuum of 29 in., and the residue from this second distillation was a thick, very viscous substance, dark in colour and possessing a strong unpleasant odour which was quite different from the harder resin obtained from the solvent naphtha fraction (b.p. 160—180° C.) used above. The yield of this viscous material amounted to 1·9 per cent of the solvent naphtha taken.

An interesting observation on the unsaponifiable nature of the coumarone resin was made with one of the harder samples obtained in this investigation. Solutions of the resin in benzol, &c., were applied to glass to form a thin film of the resin and when dry the plates were immersed in a liquid made by agitating Portland cement with water during the setting period. A thin paste of the cement and water was obtained in this way which was alkaline in reaction. The effect of this alkaline extract on the coumarone resin film was compared with the results obtained by similar treatment of films of drying oils and acid resins. In the case of the saponifiable bodies, the destructive effect of the alkali was quickly observed, but with the films of coumarone resin no disintegrating action was noticed even after exposure to the alkaline liquid for a period of several days. The films clouded and in some cases turned white, but the hardness and integrity of the coating did not appear to be affected. This property of the resin is of interest in connection with the production of a coating for concrete and stucco which is entirely resistant to the action of concrete alkali (see U.S. Patents to Ellis, Nos. 999, 439, 999, 708, and 1005, 818).—*Journal of Industrial and Engineering Chemistry*, 1916, viii., 797.

Messrs. John Wheldon and Co.'s Catalogue.—Messrs. John Wheldon and Co., of Great Queen Street, W.C., have acquired the library of the late Dr. Andrea Angel, who lost his life in the recent explosion at Silvertown, and their latest catalogue of books gives details of the books it contains, which include some valuable modern works. The catalogue also contains lists of books on mineralogy, mining, and geology from various sources, some of them being old and rare works, while others are quite modern. The considerable reduction in the prices of some of the works offers scientific men an opportunity of acquiring a valuable collection of books for a moderate outlay.

EXPERIMENTAL NOTES ON THE PREPARATION OF FIRE-PROOF WRITING PAPER.

By ROLLIN G. MYERS.

The writer made a careful study of the methods for the preparation of fire-proof writing paper, as well as of the character of the paper obtained by such processes. He extended this work to include the paper produced from crysotile fibre when this was combined, as pulp, with white or lightly tinted precipitated compounds of the metals. These pulps were prepared at about 100° C.

The method used in the preparation of the paper was identical, in many respects, to that employed by the Japanese in the preparation of their hand-made paper from the vegetable and animal fibres. Each sample prepared was tested for porosity, tensile strength, and permanence to temperatures varying from 900—1000° C. during a period of about ten hours; 80 or 90 samples of paper were prepared.

The following inferences appear to be truthful interpretations of the experimental studies:—

1. The commercial varieties of crysotile fibre used as raw material in the preparation of the paper were not to be distinguished in respect to mutability at high temperature, porosity, tensile strength, and flexibility.

2. Within certain limits, variations in the quantity of the chemical reagents used for a given weight of fibre produced no observable gain in tensile strength and the reduction of porosity in the paper prepared.

3. Tensile strength and closeness of texture of the paper prepared appears to be obtained best from pulps containing precipitated hydroxides, arsenites, silicates, and tungstates. Perhaps the best paper prepared, in respect to the properties referred to, was that obtained from a pulp containing a considerable excess of magnesium arsenite in an alkaline mixture. This paper was far in advance of any of the commercial papers examined.

It might be well to note that most of the above precipitates are flocculent in character, and that increase in closeness of texture and tensile strength is not always concurrent.

4. Substances like kaolin or pulverised mica, when incorporated with the pulps, do not seem to add anything to the paper produced.

5. In all the pulps there exist a certain amount of adhesion between the fibre and the precipitated substance. This attraction is greatest for the precipitated salts of the more basic metals like calcium and magnesium, and least for the more acid metals like silver or lead. This adhesive effect may be due to some chemical action between the fibre and the precipitate.

6. The degree of porosity of all samples increased rapidly when they were heated for any length of time above 100° C., the cause of the increase of porosity being undoubtedly the contraction to bulk of the precipitated substance in the paper.

7. Tensile strength, and smoothness of surface only, seem to be enhanced by pressing with a warm iron.

8. From the identity of crysotile to "true asbestos" and the general character of the foreign substances used, the indications are pretty clear that no foreign substance either acting by itself or with others can increase the chemical stability of asbestos towards fire.

9. *Under the experimental conditions set for the heat or "fire test," i.e., a temperature varying from 900 – 1000° C. with a time interval of ten hours, it seems probable that no paper composed of incombustible substances containing molecular water is fire-proof or can be made fire-proof.* This inference *can be extended to "true asbestos"* on account of its general similarity in properties and composition to crysotile.

It *is true*, however, that several samples of paper prepared by the writer were not seriously impaired when exposed to a dull red heat for an hour or so. These samples still possessed considerable flexibility, and could be handled, if a certain degree of care was used. There are some varieties of "true asbestos" which cling to their zeolitic(?) water with a great deal more persistence than crysotile. Paper made from asbestos of this sort would, of course, be quite well adapted for the preparation of, *e.g.*, fire-proof records. In general, then, when lower temperatures and shorter time limits are considered, it is very probable that an entirely satisfactory fire-proof paper can be prepared.

10. In respect to fire-proof inks, solutions of ferric, chromic, and cobaltous nitrates and chlorides were used. They stood the "fire test" well. According to Franz Cirkel in the Canadian Government bulletin, "Asbestos —Its Exploitation and Uses," no inks up to that time prepared would stand a red heat- excepting, perhaps those produced from platinum. For inks other than those prepared from platinum, one condition seems to be necessary, that the acid oxides in the paper should be kept in excess—*Journal of Industrial and Engineering Chemistry*, viii., No. 10.

CORRESPONDENCE.

LIBRARY CATALOGUE OF CHEMICAL JOURNALS.

To the Editor of the Chemical News.

Sir,—In your issue of August 17, 1917 (p. 84), you have a paragraph on "Library Catalogue of Chemical Journals." This paragraph contains an important mistake which I would be obliged if you could correct.

The catalogue is being produced by the Council of the Society of Chemical Industry. The Liverpool University has absolutely nothing to do with it; but as I am Secretary of the Committee which is preparing the catalogue, and as I work at this University, enquiries concerning it must naturally be addressed here.

All credit for the idea of the catalogue belongs to the Society of Chemical Industry.—I am, &c.,

Alfred Holt.

The University, Liverpool.

MISCELLANEOUS.

Sand-blended Portland Cement.—A recent bulletin of the School of Mines and Metallurgy of the University of Missouri (vol. iii., No. 3) contains a report of a valuable piece of work which has recently been brought to a state of partial completion by Prof. Edgar S. McCandliss, the Assistant Professor of Civil Engineering. The object of the investigation described was to find out whether Portland cement can be blended with sand to produce a cement having the same general physical properties as Portland cement, what amount of sand can be used without materially impairing the strength of the mixture, and whether in grinding cement clinker the introduction of sand facilitates fine grinding. About 3000 test specimens for tension were prepared, and the investigation was carried out with great thoroughness and care. The results so far obtained show that in certain circumstances as much as 40 per cent by weight of sand can be mixed with Portland cement, to produce a material which will satisfactorily pass the requirements of the present standard specifications of the American Society for Testing Materials.

Swiss Dye Industry.—A report has been issued by the Basle Chamber of Commerce dealing briefly with the position of the dye manufacturing industry in Switzerland. It seems that all the firms formerly engaged in the production of coal tar dyes have had to enlarge their plant in order to manufacture the intermediate products used in the industry, most of which had previously been imported from Germany. The supply of raw material seems to be the chief cause of anxiety, but reference is made to the assistance given by the British Board of Trade in facilitating the transport of crude tar products from that country to Switzerland. The various colour makers are making negotiations with a view to erecting a large plant for the production of mineral acids. The report further states that synthetic indigo has been produced on a small scale only, owing to the difficulty of obtaining raw materials, but it has been found possible, notwithstanding, not only to supply the demands of the Swiss market but also to export a moderate amount. Owing to complaints raised by Swiss dyers that they were not receiving a fair share of the output, the dye-stuff manufacture has been placed under the control of the Government to some extent, and export licenses are now necessary. These are granted only to countries which are supplying raw material to Switzerland, and the amount of colour exported is in proportion to the amount of raw material supplied. At the present time and under these conditions, England is the only country receiving dyes in any quantity.—*Journal of Industrial and Engineering Chemistry*, viii., No. 10.

Iron and Steel Institute.—Autumn Meeting, 1917.—The Autumn Meeting of the Institute will be held, by kind permission, at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, September 20 and 21, 1917, commencing at 10.30 a.m. on the 20th and at 10 a.m. on the 21st. The following is the programme of proceedings:—

Thursday September 20 (*at* 10.30 *a.m.*).

General Meeting of Members.

Scrutineers will be appointed for the examination of voting papers for election of new Members of the Institute.

A selection of papers will be read and discussed (Nos. 1, 4, 5, 9, 2).

Friday September 21 (*at* 10 *a.m.*).

General Meeting of Members.

A selection of papers will be read and discussed (Nos. 10, 6, 7, 3, 8).

The following is the list of papers that are expected to be submitted for reading and discussion:—

1. G. Barrett and T. B. Rogerson—"Present Practice in Briquetting of Iron Ores."
2. W. J. Brooke and F. F. Hunting—"Microstructure of Commercially Pure Iron between Ar_3 and Ar_2."
3. E. D. Campbell and W. C. Dowd—"The Influence of Heat Treatment on the Electrical and Thermal Resistivity and Thermo-electric-potential of some Steels."
4. G. Charpy and A. Cornu-Thenard—"New Impact Testing Experiments."
5. J. E. Hurst "Heat Treatment of Grey Cast-iron."
6. E. F. Law—"Effect of Mass on Heat Treatment."
7. T. D. Morgans and F. Rogers—"Investigation upon a Cast of Acid Open-hearth Steel."
8. F. Rogers—"The Acid Open-hearth Process."
9. J. H. Whiteley—"The Eggertz Test for Combined Carbon in Steel."
10. E. B. Wolff—"Failure of Boiler Plates in Service and Investigation of Stresses occurring in Riveted Joints."

Members intending to take part in the discussion of any of the papers can be supplied with copies a week before the meeting, on application to the Secretary. Copies of all papers will be available at the meeting for the use of members, and those who are unable to attend can subsequently be supplied, on application, with any paper of which copies remain.

THE CHEMICAL NEWS
VOL. CXVI., NO. 3015.

(STUDENTS' NUMBER).

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

CANDIDATES for any Degree in this University must either have passed the Matriculation Examination in this University, or be admitted under the Statute which provides that the Senate may admit graduates of or persons who have passed the examinations required for a degree in other Universities approved by it. This and all other Examinations of the University, together with the Prizes, Exhibitions, Scholarships, &c., are open to Women upon exactly the same conditions as to Men.

There are three Examinations for Matriculation in each year; commencing on the second Monday in September, January, and June or July, as may hereafter be determined.

Every Candidate for the Matriculation Examination must apply to the Principal for a Form of Entry on or before August 20, which must be returned fourteen days before the commencement of the September Examination; or must apply for a Form of Entry on or before November 25, which must be returned on or before December 1, for the January Examination; or must apply for a Form of Entry on or before April 25, which must be returned on or before May 1, for the June (or July) Examination; accompanied in each case by the proper Fee, and by a Certificate showing that the Candidate will have completed his Sixteenth Year on or before January 14 for the January Examination, July 31, the end of the Secondary School Year, for the June Examination, and September 15 for the September Examination.

Every candidate entering for the Matriculation Examination must pay a Fee of £2.

Intending Students (Internal and External) should obtain the "Regulations and Courses" from the Registrar, University of London, South Kensington, S.W.

Several valuable Scholarships and Exhibitions are available to students.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry—W. H. Perkin, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years. Students of Chemistry can obtain the degree of B.A. by passing preliminary examinations in Arts and in Science, and a final Honour examination in Chemistry. Chemistry may also be taken as part of the examination for a Pass degree. Graduates of other Universities and other persons suitably qualified can obtain the degree of Bachelor of Science after an approved course of study or research and two years' residence.

University Laboratory.—The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

There are also laboratories which specialise in different parts of the subject:—*Physical Chemistry*, Balliol and Trinity College Laboratory. *Inorganic Chemistry*, Christ Church Laboratory. *Quantitative Analysis*, Magdalen College Laboratory, Jesus College Laboratory. *Organic and General Chemistry*, Queen's College Laboratory.

Numerous Scholarships, usually of the value of £80 per annum and tenable for four years, are offered every year by the various colleges. They are awarded after a competitive examination in the various branches of Natural Science.

More detailed information may be obtained from the Examination Statutes; the Student's Handbook to the University; and from the professors and college tutors.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry—William J. Pope, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy—Sir James Dewar, M.A., F.R.S.

Goldsmiths Reader in Metallurgy—Charles T. Heycock, M.A., F.R.S.

The Student must enter at one of the Colleges or Hostels, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous examination in Classics and Mathematics, which may be done in any term of residence or before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

A graduate of another University may be admitted as a Student of Research, and obtain a degree after two years' residence in the University, by presentation of a thesis describing original research.

Facilities for research work are provided both in the Chemical Laboratories and in the Metallurgical Laboratories.

The scholarships, ranging in value from £20 to £100 a year, are chiefly given for mathematical and classical proficiency. Scholarships, or Exhibitions, are given for Natural Science at the several Colleges; the dates of the examinations vary, but are always fully advertised.

The Chemical Laboratories of the University are open daily for the use of the Students. The Demonstrators attend daily to give instruction. A list of the lectures and practical courses is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrary, Cambridge, from the *Cambridge University Calendar*, or from the "Students' Handbook to Cambridge."

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry—Sydney Young, D.Sc., F.R.S.

Professor of Applied Chemistry—Emil A. Werner, Sc.D., F.C.S., F.I.C.

Demonstrator—W. C. Ramsden, F.C.S.

Junior Demonstrator—W. Fearon, B.A.

The general Quantitative and Research Laboratories include working accommodation for about 130 Students. The Laboratories will open on October 1st. Lectures will commence on November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The Lectures delivered are:—

1. *Inorganic Chemistry and Chemical Philosophy.*—Elementary, first year; Advanced Inorganic Chemistry, second year; Physical Chemistry, third year.
2. *Organic Chemistry.*—General, second year; advanced, third year.
3. *Metallurgy.*—A Course for Engineering and Technical Students.
4. *Agricultural Chemistry.*—Theoretical and Practical Courses.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins early in April and terminates about the middle of June.

A special course for Dental Students will be given.

The University of Dublin grants the Degree of Doctor of Science to graduates of Master's standing whose independent researches in any branch of Science are of sufficient merit.

The University also grants the Degree of Bachelor of Science to graduates who have obtained Moderatorship or an Honours Degree equivalent to Moderatorship and have devoted a year to research in the University Laboratory.

By recent decrees, Prizes in Chemistry and Physics will be given in future at the October (Arts) Entrance Examination, and also at the Terminal Examinations of the Junior and Senior Freshmen Years.

Similarly, two Science Scholarships will be obtainable by Undergraduates, and tenable for five years. The Foundation Scholars receive £20 per annum, they have free commons, and their chambers for half the charge paid by other students; their tutorial fees are at one-fourth the usual rates.

KING'S COLLEGE.

(University of London).

Professors — Herbert Jackson, F.R.S., &c. (Daniell Professor), and A. W. Crossley, Ph.D., F.R.S., &c.

Assistant Professor—P. H. Kirkaldy, F.I.C., &c.

Lecturers and Demonstrators—S. W. Collins, B.Sc., L. E. Hinkel, B.Sc., H. W. Cremer, B.Sc., Herbert Savage, and A. H. Jay, B.Sc.

The Academical Year consists of Three terms. The days fixed for the commencement of Terms in 1917-1918 are Oct. 3, Jan. 16, and May 1.

The general Courses of Lectures on Chemistry deal with the nature and scope of the subject and the principles involved, in relating to one another the experimental facts, shown as illustrations of the properties of the elements and their chief compounds. The non metallic elements are first treated of, as demonstrating most clearly the characters of the interactions between the different kinds of matter, and as affording the best opportunity of classifying the main groups of compounds met with, when dealing with the inorganic branch of the subject. The metallic elements and their compounds are then discussed, and this part of the Course is completed with a *résumé* in which the connected relations of the properties of the elements are described. The latter portion of the Course embraces in the same manner a study of the principles and properties of the carbon compounds which are examples of the main groups of organic substances. Class Examinations are held from time to time during the Session.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till five daily, except Saturday.

In addition to the Laboratory Fee, each Student defrays the expenses of his own experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

For fuller details the separate Syllabuses provided for each class should be consulted.

UNIVERSITY COLLEGE.

(University of London).

Professors—J. Norman Collie, Ph.D., F.R.S. (Organic Chemistry); F. G. Donnan, M.A., F.R.S. (Inorganic and Physical Chemistry).

Assistants— S. Smiles, D.Sc.; Katharine A. Burke, B.Sc.; R. E. Slade, D.Sc.; W. B. Tuck, D.Sc.; Irvine Masson, M.Sc.; H. Terrey, B.Sc.

The Session is divided into three Terms, as follows:—First Term, from October 1 to December 19; Second Term, from January 15 to March 27; Third Term, from April 30 to July 4.

Introductory Course of Inorganic Chemistry.

Tuesday and Thursday, at 11. Practical, Thursday, 2 to 3 30, or 3 30 to 5. Fee, £10 10s.

The principles of Elementary Inorganic Chemistry, illustrated chiefly by reference to:—Air, water, salt ores, fuels, coal industry, furnace products, soda industry, mortar, cement, glass making, nitre and nitrogen fixation; other technical processes, and the properties of metals.

Junior Course of Inorganic Chemistry.

An Introduction to the Principles of Inorganic Chemistry. Special attention will be paid to general points of view, and to the application of physico chemical laws and methods.

First and Second Terms: The Class meets on Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Third Term: Lectures will be given on Mondays and Fridays at 9, and Wednesdays at 11.

Fees: Course, £7 7s.; First or Second Terms, £4 4s.

A Practical Class will meet throughout the Session.

Senior Course of Physical Chemistry.

Tuesday and Thursday at 9.

A general Course on Physical Chemistry and its applications.

Fee:—Course, £5 5s.

General Course of Organic Chemistry.

Monday and Wednesday at 12, Thursday at 3.

Fees:—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course will be held twice a week throughout the Session for those engaged in prosecuting research in Organic Chemistry. Monday and Friday at 11. Fee, £5 5s.; Term, £2 2s.

Practical Classes.

Practical Classes in Inorganic and Organic Chemistry are conducted by the Assistants.

Laboratories of General and of Organic Chemistry.

The Laboratories are open daily from 9 a.m. to 5 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week:—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

When accompanied by, or preceded by, attendance on the Lectures and Practical Classes in Inorganic and Organic Chemistry, the Laboratory Courses qualify Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

Certificates of Honour are granted to competent Students on the work done during the Session. Several valuable Scholarships are available to students.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY.

Emeritus Professors—Sir W. A. Tilden, D.Sc., F.R.S., and Sir T. E. Thorpe, C.B., F.R.S., &c.

Professor and Director of the Chemical Laboratories.—H. Brereton Baker, D.Sc., F.R.S., &c.

Professor of Chemical Technology and Fuel Chemistry—W. A. Bone, F.R.S.

Professor of Organic Chemistry—J. F. Thorpe, F.R.S.

Professor of Physical Chemistry—J. C. Philip, M.A., D.Sc.

Assistant Professor—B. Mouat Jones, M.A., D.S.O.

The Imperial College of Science and Technology, incorporated under the Royal Charter of July 8, 1907, is an institution or group of associated colleges with its principal seat at South Kensington.

The purposes of the Imperial College are to give the highest specialised instruction, and to provide the fullest equipment for the most advanced training and research in various branches of science, especially in its application to industry; and to do all and any of such things as the Governing Body consider conducive or incidental thereto, having regard to the provision for those purposes which already exists elsewhere.

For these purposes, the Governing Body, subject to the provisions of the Charter, are to carry on the work of the Royal College of Science, and the Royal School of Mines, and may establish Colleges and other Institutions or Departments of Instruction. Any Institution or Department so established, and, subject to the conditions of the Charter, the Central Technical College of the City and Guilds of London Institute, are to be integral parts of the Imperial College; and the Central Technical College is to be called and known in future as the City and Guilds College.

The Charter further provides that the Imperial College shall be established in the first instance as a School of the University of London. Students of the Imperial College who have matriculated at the University of London may therefore proceed to the Science degree of the University as "Internal Students."

Attention is particularly directed to the conditions of admission and to the extended facilities for Research Work.

The ordinary courses of instruction are planned so as to extend over four years, and are generally similar for all divisions during the first year, and to a less extent during the second year, after which they are specialised according to the particular course which the student is taking.

The following Diplomas are awarded to Students of the several constituent Colleges:—

The Diploma of the Imperial College of Science and Technology (D.I.C.) for advanced study or research in Pure or Applied Science.

The Associateship of the Royal College of Science (A.R.C.S.) in one or more of the following divisions:—Mechanics, Physics, Chemistry, Botany, Zoology, Geology

The Associateship of the Royal School of Mines (A.R.S.M.) in one or more of the following divisions:—Metallurgy, Mining.

The Associateship of the City and Guilds Institute, (A.C.G.I.) in Engineering (Civil and Mechanical), Engineering (Electrical).

Twelve entrance scholarships are given in September each year, and post graduate scholarships are available for enabling fourth and fifth year students to complete their courses. Three Research Fellowships, founded by Mr. Otto Beit, of £150 a year, tenable at the Imperial College, are offered annually to post graduate students of this College, as well as to graduates of other Universities.

Full details can be obtained from the College Calendar published by Eyre and Spottiswoode (or through any bookseller), price 6d.

THE SCHOOL OF PHARMACY OF THE PHARMACEUTICAL SOCIETY OF GREAT BRITAIN.

Professors—Chemistry, Henry L. Smith, B.Sc., F.I.C.; Pharmaceutics, Henry G. Greenish, F.I.C., F.L.S. (Dean)

A Course of Lectures on Physical, Inorganic, and Elementary Organic Chemistry, Botany, Materia Medica, and Pharmacy commences in October and terminates at the end of June. An Advanced Course of Lectures begins in October and extends to the end of March. These Lectures are adapted to the requirements of Pharmaceutical and Medical Students, and also of those who are proceeding to degrees at the University of London, or who are preparing for the examinations of the Institute of Chemistry.

Entries may be made for single classes. Certificates of attendance at the Lectures and Practical Work in Chemistry and in Botany are accepted as evidence of scientific training by the Institute of Chemistry in connection with the Examinations for the Associateship. Certificates of attendance at the Lectures and Practical Work in Chemistry are accepted by the Conjoint Board of the Royal Colleges of Physicians and Surgeons, as well as by other examining bodies. Certificates of attendance at the Course of Pharmacy are also accepted by the Conjoint Board, and at the Courses of Pharmacy and Materia Medica by the University of London for the Second Examination for Medical Degrees, Part II

Prospectuses and further information may be obtained from the Dean of the School, 17, Bloomsbury Square, London, W.C.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

University of Wales.

Professor—A. Findlay, M.A., D.Sc. (Aberdeen), Ph.D. (Leipzig), F.I.C.

Lecturer and Demonstrator—T. Campbell James, M.A., Trinity College, Cambridge, D.Sc. (Wales).

Assistant Lecturer and Demonstrator—Vacant.

Lecture Assistant—(Vacant).

Student Assistant—(Vacant).

Lecturer in Agricultural Chemistry—J. Jones Griffith, B.Sc. (Wales).

The College is open to men and women students above the age of sixteen years. The Session commences on Oct. 3rd, on which day all Students will be expected to meet the Professors in the Examination Hall of the College.

Lecture Courses.—(1) Intermediate Science Course; four lectures weekly throughout the Session. (2 and 3), B.Sc. Courses; A, three lectures weekly on Organic Chemistry; B, three lectures weekly on General and Physical Chemistry. (Courses A and B will generally be given in alternate Sessions; for 1917-1918, Course B). (4 and 5) Courses in Agricultural Chemistry. For students in their first year, 3 lectures, and for those in their 2nd year, 2 lectures weekly during the Michaelmas and Lent terms.

Laboratory Courses.—The Laboratories are open daily from 9 a.m. to 1 p.m. and from 2 to 6 p.m., Saturdays 9 a.m. to 1 p.m. Regular Courses of practical work, suitable for the B.Sc. degree of the Universities of London and Wales, or for the Associateship of the Institute of Chemistry, can be followed. Facilities are given for Students wishing to undertake research work. Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged, as far as possible, to suit the requirements of the individual Student.

The College is recognised by the University of Edinburgh and the Royal University of Ireland, and by the Colleges of Physicians and Surgeons of England, Scotland, and Ireland as an institution at which the instruction necessary for their respective Diplomas in Medicine, in Chemistry, Physics, and Biology may be given. One year for graduation in Medicine and two years for graduation in Science may be spent at Aberystwyth.

Fees.—The Fee for the whole Session, if paid in advance, is £17. This composition fee enables the Student to attend any or all the Classes and Laboratories of the College.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at examinations which commence on September 19, and exhibitions are awarded at the end of the Session on the results of the class examinations.

Intending Students requiring further information are recommended to write to the Registrar for a copy either of the General Prospectus or of one of the Special Prospectuses issued for the Agricultural and Normal Departments.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

A Constituent College of the University of Wales.

Chemistry.—Professor, K. J. P. Orton, M.A., Ph.D., F.I.C. Assistant Lecturers and Demonstrators, J. O. Hughes, B.Sc., Sybil M. Leslie, M.Sc., Lecturer in Agricultural Chemistry, H. E. Jones, B.A., B.Sc.

Physics.—Professor, E. Taylor Jones, D.Sc. Assistant Lecturers and Demonstrators, A. H. Ferguson, M.A., D.Sc., and W. E. Williams, B.Sc.

The Session opens October 2nd, 1917. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Intermediate Course.—Inorganic Chemistry and Elementary Physical Chemistry. Fee for the Session, £5.

B.Sc. Course.—Inorganic Chemistry. Fee for the Session, £3 15s. Advanced Lectures on Organic Chemistry, £1 5s. Physical Chemistry, £1 5s.

Agricultural Chemistry.—Fee, £2 10s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 5 p.m. for instruction in Chemical operations and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; Composition Fee for all Lectures and Laboratory Classes of the Science Degree Course taken in one year, £16.

The College Courses are arranged with reference to the Degree Courses of the University of Wales (of which the College is one of the Constitutent Colleges). The Courses in Science are also suited to the requirements of Students preparing for the Science Degree Course of the University of London.

The Chemistry, Botany, Zoology, and Physics Courses are recognised for Medical graduation in the Universities of Edinburgh and Glasgow, and by the Conjoint Boards of the Royal Colleges of Surgeons and Physicians, and students can make one *Annus medicus* at the college. Students are prepared for the First Examination of the Universities mentioned, the First Examination for Medical Degrees of the University of London, and of the Conjoint Board of the Royal Colleges of Surgeons and Physicians. The Science Courses are recognised for part of the science degree course of the University of Edinburgh.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE, CARDIFF.

Professor of Chemistry—C. M. Thompson, M.A., D.Sc., F.C.S.

Assistant Professor—E. P. Perman, D.Sc., F.C.S.

Lecturer to Medical Students and Demonstrator—F. W. Rea, B.A., M.Sc.

Professor of Metallurgy—A. A. Read, D.Met., F.I.C.

The Session commences October 9th and terminates on June 28th, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 30 lectures, and will cover the subjects prescribed for the Matriculation examinations of the University of Wales and the University of London.

The Intermediate Course consists of about 80 lectures; together with laboratory practice it forms the qualifying course for the Intermediate Examination of the University of Wales, and will cover the subjects required for the Intermediate Examination in Science (Part I.) of the University of London.

The Senior Course consists of about 80 lectures on Organic Chemistry.

A course on Inorganic Chemistry will be given in the Session 1918—1919

In the laboratory each student works independently, so that the course of study may be adapted to the requirements of the individual. Hours, 9 to 1 and 2 to 5; Saturday, 9 to 1. Fees—Six hours per week, £4 per session; eight per week, £6 6s. per session; twelve hours or more per week, £8 8s. per session.

Registered medical students can prepare for the Intermediate M.B. Examination of the University of London, and spend three out of their five years of medical study in Cardiff. Medical students preparing for a Conjoint Board Surgical and Medical Diploma, or for the Diploma of the Society of Apothecaries, can spend two years in Cardiff. For further information see the prospectus of the Faculty of Medicine, which may be obtained from the Registrar.

Students by making a payment of £16 at the commencement of each session may compound for all fees for the whole session.

At the entrance examination in April, and the annual examination in June, several scholarships and exhibitions are awarded. Great importance is attached to special excellence in one subject.

The College Prospectus, and also further information as to scholarships, may be obtained from the Registrar.

A special prospectus is issued concerning courses of study for diplomas in engineering, mining, and metallurgy.

A Hall of Residence for Women Students is attached to the College.

UNIVERSITY OF BRISTOL.

Department of Chemistry.

Alfred Capper Pass Professor of Chemistry—Francis Francis, D.Sc., Ph.D., F.I.C.

Lecturers—O. C. M. Davis, B.Sc., D.Sc., M.B., F.I.C.; F. W. Rixon, M.Sc., PhD.

Lecturer in Physical Chemistry—James W. McBain, M.A., Ph.D.

Lecturer in Bio-chemistry—Max. Nierenstein, Ph.D.

Lecturer in Hygienic Chemistry—Edward Russell, B.Sc., F.I.C.

Lecture Assistant—J. H. Sturgess.

The session commences on October 1.

The Department of Chemistry is situated in the new wing of the University Buildings in Tyndall's Park, and was opened on October 1, 1910. The Department provides accommodation for 200 students, and laboratories for work in specialised branches of Chemistry have been designed and equipped with apparatus of the most modern type. All the laboratories are supplied with electric wiring for experimental purposes, and currents of any desired voltage up to 250 volts at 50 ampères from dynamo or storage cells may be obtained throughout the Department. Higher voltages and currents are available in special laboratories, for Physical Chemistry and Electrometallurgy. Special facilities are afforded to those who desire to carry out research or to study Chemistry as applied to the different processes employed in the arts and manufactures; and a laboratory for Bio-chemistry has been specially designed for the investigations of problems on Biological lines.

Day Lectures.

General Courses.—1. General Inorganic Chemistry—Three lectures per week during Session and Laboratory work. 2. General Organic Chemistry—Three Lectures per week during one Session and Laboratory work. 3. Physical Chemistry—Three Lectures per week for first Session, two Lectures per week for second Session, and Laboratory work.

The Laboratories are open daily from 9.30 to 5 except on Saturdays, when they are open for Senior Students only.

Courses for Graduation.—*Intermediate Science*—Course 1 and one day Laboratory per week. *Pass Degree*—Course 2 and 3, and at least one day Laboratory per week during two Sessions. The Chemical Society must be attended during the second and third years, and one or more of the Special Courses arranged for Honours Students. *Honours Degree*—Three year course after passing the Intermediate Examination (which may be taken on entering the University). The last session is spent on research which is essential for all Honours Degrees in the Faculty of Science. During the first year in the Honours School Courses 2 and 3, and the second and third, Course 3, and one or more of the following

Special Courses as directed, *e.g.*:—Organic Chemistry, Physical Chemistry, Mathematical Chemistry, Advanced Inorganic Chemistry, Applied Electro-chemistry, some part of Bio chemistry.

The meetings of the Chemical Society must be attended during each Session.

Colloquium.—A weekly Colloquium will be held by members of the Staff to discuss recent advances in the various developments of Chemistry. Honours Students attend, and others interested are invited to do so.

Extract from Regulations as Regards Fees.

1. Registration Fee 7s. for a single Course; £1 1s. shall cover a perpetual registration for any number of Courses.

2. Inclusive Fee for an entire curriculum for degree of B.Sc., whether "Pass" or "Honours," shall be £21 a year.

3. The Fees for separate Courses of Lecturers in Faculty of Science shall be at the rate of £1 1s. per term, or £2 2s. a year for each hour per week for which the Course in question is offered.

The Fees for separate Laboratory practice and instruction in the Faculty of Science shall be at the rate of £2 2s. per term for each day in the week for which admission in the Laboratories is sought, with a minimum of £3 3s. in each particular case.

All communications to the University to be addressed to the Registrar. Information concerning Courses or Laboratory work in the Department of Chemistry may be obtained from the Professor.

The department of Experimental Physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratories. The Department of Engineering is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, mining, or motor car engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the University into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Faculty of Medicine of the University. Several Scholarships are tenable at the University.

MERCHANT VENTURERS' TECHNICAL COLLEGE, BRISTOL.

CHEMISTRY.

Professor—J. Wertheimer, B.A., D.Sc., F.I.C., F.C.S.

Lecturers—H. A. M. Borland, A.R.C.S.; Annie M. Herbert, B Sc.

Demonstrators—H. D. P. Davies and W. J. Gibbs.

Assistant in Chemical Laboratory—R Dawe.

The following Evening Classes in Chemistry are held:—Preliminary Inorganic, Mondays, 7.10—9.15; Matriculation (Inorganic), Fridays, 7.10—9.50; Intermediate (Inorganic), Tuesdays, 7.10—9.50. They will begin on Monday, Sept. 24th, 1917.

Further detailed information may be obtained from the College Calendar, price 6d., or the Prospectus for Day or Evening Classes (1d. each).

UNIVERSITY OF BIRMINGHAM.

Professor—Percy F. Frankland, Ph.D., Sc.D., LL.D., F.R.S., F.I.C.

Assistant Lecturers and Demonstrators — Hamilton McCombie, M.A., Ph.D., B.Sc., A.R.C.S., A I.C.; S. R. Carter, M.Sc.; A. Parker, D.Sc.; Wm. Wardlaw, M.Sc.; J. E. Coates, M.Sc.

Professor of Metallurgy—Thomas Turner, M.Sc., A.R.S.M.

The Session will be opened on October 2nd, 1917.

The Chemical Department has hitherto been housed in the new University buildings at Bournbrook, but owing to those buildings having been taken over by the Military Authorities for use as a Base Hospital the classes during the coming Session will be arranged for at the Birmingham Municipal Technical School and the Mason College.

Lecture Courses.

First Year.—A This part of the course is arranged (1) to give a full exposition of the general principles of Chemical Science, (2) for the systematic study of the properties of the more important elements and their compounds, and (3) to indicate the chief applications of Chemistry in the Arts and Manufactures. Three hours weekly during the Winter and Spring terms. Mondays, Wednesdays, and Thursdays at 9 30 a m. Fee, £5 5s. B. This part of the course includes an introduction to the study of Organic Chemistry, with a description of the properties, relations, and methods of preparation of the more important groups of Carbon Compounds. Three hours weekly during the Summer term. Mondays, Wednesdays, and Fridays, at 9 30 to 10 30 a.m. Fee, £1 11s. 6d.

Second Year. — *Advanced Organic Chemistry.*— This course extends over two years, and is divided into two parts:—(*a*) Carbon Compounds of the Fatty Series; (*b*) Aromatic and other Cyclic Compounds. Only one of these parts will be taken in each year. The class meets twice weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. *Advanced Inorganic Chemistry.*—This course is devoted to the consideration of special branches of Inorganic Chemistry, and direction is also given as to the private reading which should be pursued by students. The class meets by arrangement once weekly during the Session. Fee, £1 1s.

Third Year.—A further Course in Advanced Organic Chemistry will deal with one of the above parts of the Course. The class meets two hours weekly by arrangement during the Winter and Spring terms. Fee, £2 2s. A Course on Physical Chemistry. Fee, £2 2s.

The class meets two hours weekly during the Winter and Spring Terms.

Fourth Year.—For students preparing for the B.Sc. degree with Honours in Chemistry.

Special Courses in General, Organic, and Physical Chemistry.

Practical Chemistry.

The instruction in Practical Chemistry Inorganic, Organic, and Physical) extends over four years in the case of the Honours Degree. The Laboratory will be open daily from 9 30 to 5, except Saturdays, when it closes at 1 p.m. Fees—

	All day. Guineas.	Three hours per day. Guineas.	Three hours per day; five days a week. Guineas.	Three hours per day; three days a week. Guineas.
One Term ..	7	4½	4	2½
Two Terms .	13	8½	7¼	5
Three Terms	18	12	11	6¼

Special facilities are given to Advanced Students for the prosecution of original research.

Metallurgy.

There is a separate University department for Metallurgical students in which provision is made for instruction in assaying, &c.

Scholarships.

Priestley Scholarships.—Three Open Scholarships in Chemistry of the value of about £96 each are awarded annually in June.

Ascough Scholarship.—One Open Scholarship of the value of about £30 is awarded annually in July.

Bowen Scholarship.—One Open Scholarship in Metallurgy, value about £96. is awarded annually in June.

For particulars apply to the Registrar.

CITY OF BRADFORD TECHNICAL COLLEGE.

Principal—Prof. W. M. Gardner, M.Sc., F.I.C.

Department of Chemistry and Dyeing.

Professor of Chemistry and Dyeing—The Principal.

Assistant Professor of Chemistry—B. North, A.R.C.S.

Lecturers in Chemistry—L. L. Lloyd, Ph.D.; H. Middleton, M.Sc.; A. Jackson, B.Sc.; E. Jones, B.Sc.

Lecturer in Physics—J. A. Tomkins, A.R.C.S. (Lond.)

Demonstrator in Physics—F. Harcourt, B.S.

Lecturer in Gas Manufacture—J. W. Roper.

Lecturer in Botany—J. Cryer.

Lecturer in Pharmacy—G. H. Etchells.

Lecturer in Biology—J. A. Fisher.

The following courses of instruction are provided:—

I. *General Chemistry Course*, extending over four years, and including Lectures in Inorganic, Organic, and Technological Chemistry, Principles of Analysis, Technical Analysis, Electro-chemistry, Physical Chemistry, Physics, Mathematics, Mechanics, with Laboratory work in Chemistry and Physics.

II. *Chemistry and Dyeing Course*, extending over four years. Includes most of the above subjects, along with Lectures and practical work in Dyeing, Colour matching, &c. The practical laboratories include a completely equipped Practical Dyehouse and Finishing Rooms.

III. *Chemical Engineering.* Three years' course, preparing Students for positions in Chemical Works, Sewage Works, &c.

IV. *Sanitary Science.* One year's Course, recognised by the Sanitary Institute as preparing for their certificate examination. Subjects: Chemistry, Physics, Sanitary Engineering, Sanitary Law, Building Construction, Drawing, Physiology, and Bacteriology.

V. *Dyeing.* Special Courses for Graduates in Chemistry, and for Drysalters, Colour Merchants, &c.

VI. *Textile and Dyeing.* Arranged for those Students who desire to study the two subjects simultaneously.

VII. *First Professional Examination, Conjoint Medical Board (M.R.C.S., L.R.C.P.), London.*—Attendance at the College and College Certificates in Chemistry, Physics, and Biology are recognised by the Conjoint Boards for Medical Studies (London and Dublin) as a qualifying curriculum.

VIII. *General Pharmaceutical Course.* Prepares for the Minor, Major, and Assistants' Pharmaceutical Examinations. Each extends over two years on four half-days per week, and includes Chemistry and Physics, Botany, Biology, Materia Medica, Pharmacy, and Dispensing.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor—Prof. E. Kinch, F.C.S., F.I.C.
(Closed during the period of the war).

THE UNIVERSITY OF LEEDS.

Professor of Chemistry—Arthur Smithells, B.Sc., F.R.S.

Professor of Organic Chemistry—Julius B. Cohen, Ph.D., B.Sc., F.R.S.

Lecturer on Physical Chemistry—H. M. Dawson, D.Sc., Ph.D.

Lecturer in Analytical Chemistry—W. Lowson, B.Sc., F.I.C.

Assistant Lecturer and Demonstrator—W. H. Perkins, M.Sc.

Temporary Demonstrator—F. W. Turner, B.Sc.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m. Fee for the Course, £5 10s.

2. Advanced Inorganic Chemistry.—(A) Monday, Wednesday, and Friday, at 9.30 a.m. Fee, £4 10s.

3. Advanced Inorganic Chemistry.—(B) Tuesday, Thursday, and Saturday, at 9.30 a.m. Fee, £4 10s.

4. Organic Chemistry.—Tuesday, Thursday, and Saturday at 11.30 a.m. Fee, £4 10s.

5. Honours Courses.—(*a*) Organic Chemistry: Monday, Wednesday, and Friday at 11.30 a.m.; fee, £4 10s. (*b*) History of Chemistry: Monday, Wednesday, and Friday at 9.30 a.m. in the First Term; fee, £2 5s. (*c*) Physical Chemistry: Three hours a week at times to be arranged; fee, £4 10s. (*d*) Electro-chemistry: Tuesdays at 9.30 a.m.; £2 10s.

6. Chemistry of Food and Drugs.—Special class during the second term for Students taking Final Examination of the Institute of Chemistry in Branch E (Food and Drugs). £3 3s.

Laboratory Courses.

The University Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session.—£3 per half day of three hours per week.

Practical Course in Sanitary Chemistry.—Tuesdays and Thursdays from 2 to 5 in the Second and Third Terms. Fee, £7 7s.

Colour Chemistry and Dyeing Department.

Professor—A. G. Perkin, F.R.S., F.I.C.

Lecturer and Research Chemist—J. B. Oesch, Ph.D.

Lecturer in Dyeing and Research Assistant—P. E. King.

Demonstrator—A. E. Woodhead, M.Sc.

The Courses extend over periods of (*a*) three or (*b*) four years, and are intended for those who wish to obtain a full scientific and practical education in the art of dyeing, colour manufacture, &c. Diploma Course (*a*) is suitable for those who purpose to become dyeing chemists, and desire in the future to take part in the direction of the operations of dyeing and calico printing; *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c. Honours Course (*b*) is more largely concerned with the study of colour manufacture, and is designed for the training of factory and research chemists required by works which are engaged in the preparation of dyestuffs.

Textile Industries Department.

Professor—Aldred F. Barker, M.Sc.

Lecturer in Textile Industries—H. Priestman.

Lecturer in Yarn Manufacture—T. Hollis.

Lecturer in Textile Chemistry—W. Harrison, M.Sc.

Engaged on Special Research—S. A. Shorter, D.Sc.

Assistant Lecturers—A. Yewdall, W. Law.

The courses of instruction extend over three or four years according to the Degree or Diploma Course selected. Shortened courses are arranged for special sections of the work. The practical equipment is designed to enable workers in the department to pass wool through every process from the Raw Material to the Finished Fabric. The Research Laboratories are equipped for the Scientific Investigation of the fundamental principles underlying all the processes involved in Wool Manufacture. Clothworkers' Scholarships are at the disposal of the University, and it is very probable that under the newly developed West Riding of Yorkshire Scheme valuable Travelling Scholarships will be available for Senior Textile Students.

Leather Industries Department.

Professor—H. R. Procter, D.Sc., F.I.C.

Assistant Lecturers and Demonstrators—Harold Brumwell; W. R. Atkin, M.Sc.

Demonstrator—F. C. Thompson, M.Sc.

The full Courses, which extend over a period of either two or three years, are suitable to all who intend to become Technical Chemists in the Leather Industry, or managers of important works, and are recommended to sons of tanners. The Courses include instruction in chemistry, a modern language, leather manufacture, and practical work in the Leather Industries Laboratory and Dye house. In 1914 the capacity of the University to undertake research in this branch of Applied Science was greatly extended by the establishment, in a new building adjoining the Leather Department, of the Procter International Research Laboratory, erected by the leather industries of the world in recognition of the work of Henry Richardson

Procter, the first Professor of Leather Industries in the University.

Agricultural Department.

Professor—R. S. Seton, B.Sc.

Professor of Agricultural Chemistry—C. Crowther, M.A., Ph.D.

Assistant Lecturers in Agricultural Chemistry—W. Godden, B.Sc., A.R.C.S., F.I.C.; N. M. Comber, B.Sc., A.R.C.S.; J. A. Hanley, Ph.D.

The full Course occupies three years, and includes instruction in chemistry, physics, mathematics, geology, botany, forestry, engineering and surveying, and the principles of agriculture, as well as practical work in the various laboratories and out door agriculture at the University Farm.

Institution for Research in Animal Nutrition.

Director—C. Crowther, M.A., Ph.D.

Biochemist—H. W. Dudley, M.Sc., Ph.D.

Research Assistant—H. E. Woodman, M.Sc., Ph.D.

The Institution is maintained by a special grant from the Board of Agriculture and Fisheries, and is closely associated with the Agricultural Department of the University.

Department of Coal-gas and Fuel Industries with Metallurgy.

Livesey Professor—J. W. Cobb, B.Sc., F.I.C.

Lecturer in Gas Chemistry—H. J. Hodsman, M.Sc.

The Courses extend over two, three or four years, and are suitable for those who are preparing for posts either as Gas Engineers or in Fuel and Metallurgical industries.

The Courses in Gas Engineering and the Technology of Fuel will chiefly deal with the manufacture and distribution of coal-gas and gas-lighting problems, by-product coking processes, and the production and application of gaseous fuels for heating and power purposes.

The Metallurgical Courses, besides dealing with general processes for the concentration and extraction of ores, will be chiefly directed to problems underlying blast furnace and open-hearth steel practice, and to the microstructure, physical properties, and heat treatment of steel and other industrial alloys.

Special attention is paid to the study of Refractory Materials.

Research Students are admitted to the University Laboratories on reduced terms.

Several valuable Fellowships and Scholarships are at the disposal of the University, including a Fellowship of £100 offered by the Institution of Gas Engineers, and the Salt, Akroyd, Brown, Baines, Emsley, Craven, and Clothworkers' Scholarships, and one of the 1851 Exhibition Scholarships. The Leeds City Council's and the North, East, and West Ridings County Council's Scholarships are tenable at the University of Leeds.

UNIVERSITY OF LIVERPOOL.

Professor of Inorganic Chemistry—E. C. C. Baly, M.Sc., F.R.S.

Professor of Physical Chemistry—W. C. McC. Lewis, M.A., Ph.D.

Professor of Bio-chemistry—W. Ramsden, M.A., D.M.

Professor of Organic Chemistry—R. Robinson, D.Sc.

Assistant Lecturers and Demonstrators—A. J. Allmand, D.Sc.; Francis W. Kay, M.Sc., Ph.D.; J. Smeath Thomas, M.Sc.

Lecture Assistant—H. H. Froysell.

The Session commences early in October.

The Classes meet the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the M.Sc. or D.Sc. Degree in the University of Liverpool; for Degrees in Medicine of Liverpool; for the Pharmaceutical, Veterinary, Dental, and Public Health Diplomas; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Associateship of the Institute of Chemistry and other Examination Boards.

Lecture Courses.

A. General Introductory Course, including the principles of Organic and Physical Chemistry. Three Terms. Fee, £4.

Engineer's Course of Lectures with Practical Class. Two Terms. Fee, including Practical class, £6.

Course A.—General Elementary Chemistry, £4.

Course B.—Inorganic Chemistry. Fee, £3.

Course C.—Inorganic Chemistry (Honours Course). Fee, £4.

Course D.—Organic Chemistry. Fee, £3.

Course E.—Organic (Honours). Fee, £4.

Course F.—Physical Chemistry. Fee, £3.

Course G.—Honours Physical Chemistry. Fee, £4.

Course H.—Applied Inorganic Chemistry, £2 10s.

Course J.—Metallurgy. Fee, £2 10s.

Course K.—Applied Organic Chemistry. Fee, £2 10s.

Course L.—Electro-chemistry. Fee, £2 10s.

Also Pass and Honours Courses in Bio-chemistry.

Research students carrying out research work pay a fee of £3 per annum.

The Inorganic and Organic Chemical Laboratories provide accommodation for every kind of work and research in inorganic and organic chemistry and in metallurgy. There is also a laboratory devoted to spectroscopic work and research.

The Muspratt Laboratories of Physical Chemistry and Electro-chemistry adjoin the main chemistry buildings, and, owing to their full equipment, offer every opportunity for all manner of work and research in these subjects.

The Bio-chemical Laboratory is also separately housed, and provides facilities for work and research.

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study, for which a full curriculum is provided. Fees:—

Per Week	One Term, Three Months.	Three Terms One Session.
One day	£4	£7
Two days	5 10s.	10
Three days	7	13
Whole week	10 10s.	21

D.P.H. Course (see special syllabus).

Course for Dental Degree and Diploma (see special syllabus).

Technological Curriculum.

The curriculum extends over three or four years.

The Final Examination for the Associateship of the Institute of Chemistry may be taken after the third year. Those students who have taken the Ordinary Degree of B.Sc. may pass the M.Sc. Exam. in any subsequent year.

The Sir John Willox Scholarship of £50 per annum, tenable for two years, will be competed for in December, 1917, on an Examination in subjects which are included in the first two and a half years of the above curriculum. Candidates should send in their names to the Registrar not later than November 15. The Sheridan Muspratt Chemical Scholarship, on similar lines, is open for competition. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students. Regulations as to these may be obtained from the Registrar.

ARMSTRONG COLLEGE, NEWCASTLE-ON-TYNE.

(In the University of Durham).

Professor of Chemistry—P. Phillips Bedson, M.A., D.Sc., F.I.C., F.C.S., J.P.

Lecturers in Chemistry—F. C. Garrett, D.Sc., F.C.S. (serving with H.M. Forces), and J. A. Smythe, D.Sc., Ph.D., F.C.S.

Assistant Lecturers and Demonstrators—A. Forster, M.Sc., Ph.D. (engaged on Munition Work), J. B. Firth, M.Sc., and Miss C. B. Schofield, M.Sc.

Lecturer in Agricultural Chemistry—S. Hoare Collins, M.Sc., F.I.C., F.C.S.

Assistant Lecturer in Agricultural Chemistry—A. A. Hall, M.Sc., Ph.D. (serving with H.M. Forces).

First Year Courses.—Division I.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 3rd. Fee, £3 10s. for the Session.

Division II. Similar to Division I., but modified to meet requirements of Students for Degrees in Engineering and Mining. Mondays 12 to 1, Tuesdays and Thursdays 10 to 11. Fee, £3 10s. for Session.

Second and Third Year Courses.—These lectures are designed to form a part of the course of instruction in Chemistry, and to prepare students for the examinations in Chemistry for the degree of Bachelor of Science, Pass and Honours.

(*a*) Inorganic Chemistry.—Advanced Course. Tuesdays and Thursdays at 11 a.m. Fees, Lectures, £3 10s. per session, and £1 10s. per term.

(*b*) Organic Chemistry.—Aliphatic and Aromatic Compounds, Tuesdays and Thursdays at 10 a.m. Fees, Lectures, £3 10s per session; £1 10s. per term.

(*c*) Organic Chemistry.—Advanced Course, Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s per session; £1 10s. per term.

(*d*) History of Chemistry and Chemical Philosophy.—Saturdays at 10 a.m. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*e*) Physical Chemistry.—Tuesdays and Thursdays at 12 noon for part of the session. Fees, Lectures, £3 10s. per session; £1 10s. per term.

(*f*) Analytical Chemistry.— Fridays at 9 15 a.m. Fee, £1.

(*g*) The Rarer Elements and the Periodic Law.—Times to be arranged. Fees, Lectures, £3 10s. per session; £1 10s. per term.

Students taking Chemistry for Pass Degree will attend in their second year the course *a* and *f*, and in their third year the courses *b* and *d*, in addition to the necessary Laboratory practice.

Students taking Chemistry for Honours Degree will attend in their second year the courses *a*, *b*, and *f*, and in their third year the courses, *c*, *d*, *e*, and *g*, in addition to the necessary Laboratory practice.

A Lecture Course in Analytical Chemistry will be given on Fridays, at 9.15 a.m. Fee for the course, £1.

Metallurgy and Assaying.—Lecturer, Prof. Louis, M.A., D.Sc., F.I.C., F.G.S.; Demonstrator, H. Dean, M.Sc., A.R.C.M. A Metallurgical Laboratory is provided, in which instruction is given in the ordinary processes of Dry Assaying, and in the preparation and analysis of Alloys, &c. Fees as for Chemical Laboratory.

Agricultural Chemistry.—The instruction in this branch of Chemistry will consist of a series of Lectures and of special practical work in the Chemical Laboratory. Students will be expected to have a knowledge of Elementary Chemistry, such as may be obtained by attending the General Course.

The Lecture Course in Agricultural Chemistry is arranged for two days a week throughout the Session. Fee, £3 10s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees*.—Students working six days per week £5 10s. per term, £15 per session; one day per week, £2 per term, £5 per session.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students, who are also Members of the University of Durham; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the degree of Bachelor in Science of the University of Durham. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must have passed the University Matriculation Examination.

Matriculation Examination.—In order to enter on a course of study for a Degree a student must have previously satisfied the Examiners in the following subjects:—(1) English, (2) English History, (3) Mathematics, (4) three of the following subjects, of which one must be a language:—(*a*) Religious Knowledge, (*b*) Latin, (*c*) Greek, (*d*) Ancient History, (*e*) French, (*f*) German, (*g*) some other language to be approved, (*h*) Experimental Science or Physics or Chemistry, (*i*) Botany or Zoology, (*j*) Mechanics, (*k*) Extra Mathematics, (*l*) Geography.

(i.). Candidates for degrees in Arts, who do not offer Latin in their Matriculation Examination or in the equivalent accepted as exempting therefrom, will be required to pass in Latin at a subsequent examination before entering upon the Arts course.

(ii.). Candidates for degrees in Commerce, who do not offer a Modern Foreign Language in their Matriculation Examination, or in the equivalent as exempting therefrom, will be required to pass in a Modern Foreign Language at a subsequent examination before entering upon the Commerce course.

(iii.). Candidates for degrees in Engineering (Civil, Mechanical, and Electrical) and in Naval Architecture will be required to take the following subjects from the list:—(1) English; (2) English History; (3) one of four languages—Latin, Greek, French, German; (4) Experimental Science; (5) Extra Mathematics; (6) Geography.

(iv.). Foreign Students may be exempted from the Matriculation Examination on report from the Board of Professors of Armstrong College, that they have received such an education in their own country as will enable them to profit by University study, and that they have sufficient knowledge of English to enable them to follow the courses of instruction they are entering for.

For detailed Syllabuses and complete Regulations the College Calendar should be consulted.

Bachelorship in Science.—The degree of Bachelor of Science is conferred in Pass and Honours in Pure and Applied Science. For details of curricula, &c., the College Calendar should be consulted.

Exhibitions.—Two Exhibitions of the value of £20 and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

The examination will be held at the College, and will commence on Thursday, Sept. 27th, 1917. Candidates should send in their names to the Secretary on or before September 10th.

Several valuable Scholarships are available for students, including the Johnston Chemical Scholarship of the value of £60 for one year, which is open to Bachelors of Science of any British University; the examination for this Scholarship will be held during the week commencing October 8th. Candidates should send in their names to the Secretary on or before September 27th.

THE UNIVERSITY OF MANCHESTER.

Professor of Chemistry and Director of the Chemical Laboratories—Harold B. Dixon, M.A., M.Sc., Ph.D., F.R.S.

Professor of Organic Chemistry—Arthur Lapworth, D.Sc., F.R.S.

Reader in Biochemistry and Senior Lecturer in Chemistry—*C. Weizmann, Ph.D., D.Sc.

Senior Lecturers and Demonstrators—Norman Smith, D.Sc.; *E. C. Edgar, D.Sc.; F. P. Burt, D.Sc.; J. E. Myers, D.Sc.

Assistant Lecturers and Demonstrators—†W. J. Jones, M.Sc.; †J. R. Partington, M.Sc.; Colin Campbell, M.Sc.; H. Stephen, M.Sc.; W. K. Slater, M.Sc.; Leonora Pearson, M.Sc.

Professor of Metallurgy—C. A. Edwards, D.Sc.

Assistant Lecturer in Metallurgy—W. E. Thornycroft, B.Sc., M.Sc.

Lecturers in Electro-Chemistry—†J. N. Pring, D.Sc.; E. Newbury, D.Sc.

(* Under leave for special work for Ministry of Munitions. † Serving in H.M. Forces).

Chemistry Lecture Courses.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

This course is intended for Students commencing the study of chemistry.

Introduction to Organic Chemistry.—Mondays, Wednesdays, and Fridays, at 11.30, during the Summer Term. This course is designed to meet the requirements of Students preparing for the Intermediate B.Sc. Examination.

Biochemistry, Theoretical and Practical—Tuesdays and Thursdays during the Summer Term. This Course prepares for Part III. of the first M.B. Examination.

First Year Honours Course.—Mondays, Wednesdays, and Fridays, 11.30, during the two Winter Terms. The Non-Metals.

Second Year Honours Course.—Mondays, Wednesdays, and Fridays, at 2, during the two Winter Terms. The Metals.

Third Year Honours Course.—Theoretical and Physical Chemistry.

Organic Chemistry (*General*).—Mondays, Wednesdays, and Fridays, at 9.30, during the two Winter Terms.

Organic Chemistry (*Advanced*).—Tuesdays and Thursdays, at 9.30, during the two Winter Terms.

History of Chemistry.—Short Courses during the two Winter Terms.

Chemistry of Colouring Matters — Theoretical and Practical Course during the Winter Terms.

Metallurgy.—Introductory Course, followed by either—(A) Lead, Copper, Bismuth, Antimony, Zinc, and Tin; or (B) Iron and Steel. Course A, two Lectures per week during the first half of the Session. Course B, one Lecture per week during the Session.

Electro-chemistry.—General Theoretical Course: One hour per week during the Michaelmas and Lent Terms. Applied Course: One hour per week during Michaelmas and Summer Terms.

B.Sc. with Honours in Chemistry.—The course extends over three years, and comprises systematic instruction by means of lectures and practical work in the laboratories.

The Research Laboratories for Inorganic, Organic, and Physical Chemistry, and for Metallurgy, are open to graduates and other advanced students.

For further particulars of any of these courses apply to the Registrar, Edward Fiddes, M.A., or to the Director of the Laboratories.

UNIVERSITY COLLEGE, NOTTINGHAM.

DEPARTMENTS OF CHEMISTRY AND METALLURGY.

Professor of Chemistry—F. Stanley Kipping, Ph.D., D.Sc., F.I.C., F.R.S.

Demonstrators of Chemistry—R. M. Caven, D.Sc., F.I.C.; E. B. R. Prideaux, M.A., D.Sc.; and H. Lambourne, B.Sc.

The Classes of the College are open to students of both sexes above sixteen years of age.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student attends a course on Inorganic Chemistry. In his second year he attends Lectures on both Inorganic and Organic Chemistry. In his third year he attends courses on Advanced Organic Chemistry, Physical Chemistry, and Advanced Inorganic Chemistry.

Demonstrations and Lectures on Analytical Chemistry are given, and Chemical Calculation and Tutorial classes are also held. Various short courses of lectures on special subjects are delivered during the Session.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford, and for the Medical Examinations of the Royal College of Surgeons and of the Universities of Cambridge and Edinburgh: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry and Metallurgy.—The Chemical and Metallurgical laboratories are open every day from 9 to 5, except on Saturday, when the hours are from 9 to 1; also on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation, in Qualitative and Quantitative Analysis, and in the methods of Original Chemical Investigation and Research; Students are also enabled to work out the applications of Chemistry to Pharmacy, Metallurgy, Dyeing, Brewing, Iron and Steel, and other Manufacturing Processes.

Research Work.—Students or others wishing to undertake research work in pure or Applied Chemistry will be afforded every facility for doing so and may be admitted at reduced fees. The Laboratories are fully equipped with apparatus and chemicals necessary for such work.

Courses of Technical Chemistry Lectures are also given on Engineering, Dyeing and Bleaching, Brewing, Plumbing, Gas Manufacture, and on other processes of applied Chemistry.

Pharmaceutical Students are provided with Lectures and Laboratory work suitable for the preparation for the Minor and Major Examinations.

The composition fee for full time in the Chemistry Department (lectures and laboratory) is £6 per term, and this fee covers all necessary apparatus and chemicals.

A composition fee of £6 per term is also charged for various complete courses, such as those required for the Institute of Chemistry, and for the degree examinations of London University.

Evening Classes.—Evening Lectures and Laboratory instruction will be given in Pure and Applied Chemistry, and the laboratories are open for practical work on Tuesday and Thursday evenings from 7 to 9. Fee for each Lecture Course, 5s.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus, free from the Registrar.

THE UNIVERSITY OF SHEFFIELD.

Professor of Chemistry—W. P. Wynne, D.Sc., F.R.S.

Lecturer on Physical Chemistry—W. E. S. Turner, D.Sc., M.Sc.

Lecturers and Demonstrators—W. J. Jarrard, B.Sc.; J. Kenner, D.Sc., Ph.D.; C. R. Young, D.Sc., B.Sc.

Temporary Lecturers and Demonstrators—Emily G. Turner, M.Sc.; Dorothy M. Bennett, M.Sc.; Annie M. Mathews, M.Sc.

The Session will commence October 4th.

Matriculation Course. — Tuesday and Friday at 9.30, Wednesday at 11.30 during Michaelmas and Lent terms. Fee, £2 12s. 6d., and three hours per week Laboratory work.

Candidates for the Intermediate Examination are required to satisfy the Examiners in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, and Botany. And those for the Final Examination in three of the following subjects:—Pure Mathematics, Applied Mathematics, Physics, Chemistry, Zoology, Botany, Physiology, Geology, Education, Geography.

Intermediate Course in Chemistry for B.Sc. or M.B., Ch.B. or B.Met.—Monday, Wednesday, Thursday, and

Saturday at 9 30 a.m. £5 5s., and six hours per week Laboratory work during first year.

B Sc. Course in Chemistry.—Monday at 9 30 a m. and Friday at 12 30 p.m. during second year, £3 3s.; Wednesday at 12.30 p.m, during two terms, Monday at 12.30 p.m and Thursday at 11 30 a.m., during third year, £3 3s.; and nine hours per week Laboratory work during second and third years.

B.Sc. with Honours.—Honours Students in Chemistry, after passing the Intermediate Examination, devote the whole of their time to the study of Chemistry, and are expected to reach the standard for a pass in Chemistry for the ordinary degree by the end of the second year. During the second or third year they devote one day a week to lectures and practical work in a subsidiary subject—Mathematics, Physics, or Metallurgy—selected for the degree. The third year is devoted to the advanced study of Chemistry, either chiefly Physical and Inorganic or chiefly Organic, as the student may select. At least four days a week during the second and third years are spent in the laboratory.

M.Sc.—This degree may be conferred upon a Bachelor of Science with Honours who is of one year's standing from the date of his graduation as a Bachelor of Science, or upon a Bachelor of Science who has either passed an examination in an Honours School subsequent to graduation, or has for at least one year after graduation done research work at the University, and has presented a thesis, approved by the Faculty of Pure Science, upon the research work done during that period.

D.Sc.—The degree of Doctor of Science may be conferred upon any Master of Science of not less than five year's standing from the date of his admission to the degree of Bachelor, provided that he has published, in recognised journals or transactions, a research or researches of special merit and approved by the Faculty of Pure Science as qualifying him for the degree.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Three hours per week, £3 3s.; Six, £5 5s.; Nine, £7 7s.; Twelve, £9 9s.; Eighteen, £12 12s.; Twenty-four, £14 14s.; Thirty-two, £16 16s.; Honour or University Students taking eighteen hours or more per week, £12 12s.

Students joining the Laboratory for one term are charged one-half, and for two terms two-thirds of the Fees for the whole Session.

A Course of Lectures, with a special class in Laboratory Work, is arranged for Medical Students entering for the Conjoint Board Examinations. Fee, £7 7s.

A course of Practical Chemistry which meets the requirements of candidates for the Diploma of Public Health is held during the Michaelmas and Lent terms. Fee, £6 6s.

An arrangement has been entered into with the Board of Education, London, S.W., which will enable Science Teachers to work in the Chemical Laboratory for three, six, or twelve hours a week on payment of one-quarter of the usual fee, the Board being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar of the University.

Evening Classes.—Lecture Class and Laboratory, on Thursday evening during the Michaelmas and Lent terms. Fee, £1 10s.

FACULTY OF METALLURGY.

Dean and Professor—J. O. Arnold, D.Met., F.R.S.
Senior Lecturers—F. K. Knowles, B.Met.; F. Ibbotson, B.Met., B.Sc.
Lecturer—J. H. Wreaks, B.Met.
Demonstrators—L. Aitchison, D.Met., B.Sc.; F. C. Thompson, D.Met., B.Sc.
Lecturer in Non-ferrous Metallurgy—G. B. Brook.
Demonstrator—F. Orme, M.Met.
Lecturer in Electro-metallurgy—W. R. Barclay, A.M.I.E.E.

This Faculty has been equipped to meet the requirements of the local industries. The Laboratory is fitted with the most modern apparatus for metallurgical analysis, more especially with appliances for the rapid and accurate chemical examination of iron and steel, fuel, and refractory materials. It also contains a complete pyrometric installation, and a laboratory for the study of the micrographic analysis of metals fully equipped with specially designed microscopes by Ross, polishing tables, etching appliances, incandescent light for evening work, &c. The Faculty is now most complete for teaching the practical manufacture, the chemical constitution, and the physical properties of steel. Special attention is given to the determination of the microscopic constituents of steel. Although the chief industry of the district occupies the central position in the course of instruction, general metallurgy is dealt with in the Non-ferrous Department described below. Students are thus enabled to select and at once enter upon a course of scientific metallurgical training of immediate practical utility. They may take up and work through any portions of the course, but certificates are granted only to those who follow the prescribed courses and pass the necessary examinations. Lectures on Iron and Steel Manufacture, on Fuel and Refractory Materials, and Metallurgical Geology. Practical Metallurgy:—Laboratory, Furnaces, Foundry, and Testing Machine Course; Practical Course of Metallurgy other than Iron and Steel; Practical Fuel Course for Students in Collieries or Gas Works.

A steel works has been erected in connection with the Sheffield University at a cost of about £15,000, with a most varied and complete plant. The most recent addition to the steel works plant is a 3 cwt. Kjellin induction furnace worked by a 120 H.P. Motor-generator set with two-phase current. The Faculty of Metallurgy of Sheffield University is "in association" with the Royal School of Mines for teaching the advanced metallurgy of Iron and Steel.

There has been recently added to the curriculum Day and Evening courses in Electro-metallurgy and Non-ferrous Metallurgy. The Electro-metallurgical Laboratory is completely equipped for the practical study of every branch of the art of the Electro-deposition of metals, special attention having, however, been paid—in the selection and arrangement of plant and apparatus—to the specific requirements of the Sheffield trades. The plant and machinery is thoroughly up-to-date in character. Working accommodation is provided for 30 students at one time. The course extends over three university years.

The Non-ferrous Department has been established to meet the needs of the lighter Sheffield trades of Silver and Electro-plate, Brass, and allied industries. It is completely equipped for dealing with every phase of the work from the raw material. The melting shop is fitted with furnaces capable of dealing with casts up to 70 lbs. weight, so that commercial practice can be followed. Two large laboratories, the one with 32 places for preparatory students, the other with accommodation for 40 advanced students, provide the means for the Chemical examination of the alloys prepared. A Staff and Post graduate research laboratory completes the provision for the chemical side of the work. The Micrographic Laboratory is equipped with a complete Zeiss Photo-micrographic camera, direct driven polishing blocks, and Ross microscopes. The recalescence laboratory for the estimation of temperatures during melting, annealing, or other heat treatment has a complete pyrometric installation. An Arnold and Culver-Glauert Pyrometer permits of readings every 1° C. up to 1300° C. Facilities are provided for observing the thermal changes *in vacuo*. The Chronographic recorder is served by electric or coke furnaces, and the installation may be regarded as the most complete of its kind.

Degrees are awarded to successful students in Steel Metallurgy, and Associateships in both Steel and Non-ferrous Metallurgy.

UNIVERSITY COLLEGE, READING.

Professor of Chemistry—H. Bassett, D.Sc., Ph D., D. ès Sc., F.I.C.

Lecturer—J. W. Dodgson, B.Sc.

Professor of Agricultural Chemistry—S. J. M. Auld, D.Sc., Ph.D , F.I.C.

Research Chemist in Dairying—J. Golding, F.I.C.

Lecturer in Agricultural Chemistry—J. A. Murray, B.Sc.

The lectures and laboratory work are so arranged as to be suitable for students preparing for the London B.Sc. (Pass or Honours), or for the College or other Diplomas in Agriculture, Horticulture, or Dairying. There is a general course of Intermediate standard, also another suitable for first year students of Agriculture and Horticulture. In their second and third years Science students attend special lectures in Inorganic, Organic, and Physical Chemistry, while Agricultural students take special courses under the Professor of Agricultural Chemistry. The laboratories are well equipped for all branches of practical work.

Halls of Residence—(Men) Wantage Hall, St. Patrick's Hall; (Women) St. Andrew's Hall, Wessex Hall, St. George's Hostel.

Full details of fees, scholarships, &c., can be obtained from the Registrar.

UNIVERSITY COLLEGE, DUNDEE.

University of St. Andrews.

Professor of Chemistry—Alex. McKenzie, M.A., D.Sc., Ph.D., F.R.S., F.I.C.

Lecturer—J. K. Wood, D.Sc.

Demonstrator—(Vacant).

Lecture Assistant and Lab. Steward—J. Foggie.

The Session consists of three Terms:—The Martinmas Term begins early in October and ends before Christmas; the Candlemas Term begins early in January and ends about the middle of March; the Whitsunday Term begins in the middle of April and ends at the end of June.

Three Courses of Lectures are given, each extending through all three terms. The General Course, meeting four or five days a week (including Tutorial Meetings), is intended for beginners, and qualifies for Graduation Examinations in Arts (M.A. General), Science (First B.Sc.), and Medicine (First M.B., Ch B).

The Special and Honours Courses, each meeting twice or thrice weekly, qualify for Degree Examinations in Arts (Special and Honours, respectively), and in Science (Final B.Sc. on Intermediate and Higher Standard, respectively).

All three are General Courses, including Inorganic, Physical, and Organic Chemistry.

The Laboratories are well equipped, and instruction is provided for students in Arts, Science (Pure and Applied), Medicine (including Public Health); provision is also made for students desiring to undertake Research.

UNIVERSITY OF ABERDEEN.

Chemistry.

Professor—Frederick Soddy, M.A., F.R.S.

Lecturers—Francis W. Gray, M.A., D.Sc.; Joseph Knox, D.Sc.

I. *General Lecture Course, Systematic Chemistry.*—(Daily during the Winter Session at 3 p.m.). These lectures treat of:—(1) The Laws of Chemical Combination and the General Principles of Chemistry, including Chemical Calculations; (2) the Elements classified according to the Periodic Law; (3) Organic Chemistry; (4) Applications of Chemistry to the Arts and Manufactures. Two written Class Examinations are held. A Tutorial Class (without fee) is held in connection with the General Lecture Course. Fees, for first attendance, £4 4s; for subsequent attendance, £3 3s.

II. *Elementary Practical Course for all Students.*—(Spring Term). Demonstration on Monday at 12 noon. For practical work the class will be divided into two groups; one group will meet on Tuesday and Thursday, and the other on Wednesday and Friday, from 10 a.m. to 1 p.m. This course is devoted to practice in Chemical Methods and in Elementary Qualitative Analysis. The instruction is under the direction of the Professor of Chemistry and the Staff. One practical examination is held at the end of the course, namely, the Degree Examination, but it must be attended by all, those not sitting the Degree Examination taking it as a Class Examination. Students in all faculties are required to pass this practical examination as well as the written examination, as part of the requirements for the Degree. The practical course should be taken, whenever possible, concurrently with the Systematic course. Fee, £3 3s. This fee includes the necessary apparatus and appliances, with certain exceptions such as platinum-foil and wire.

Scheme of Lecture Courses for the B.Sc. Degree in Chemistry (subsequent to Courses I. and II.).

III. (*a*) Introductory Physical Chemistry, 15 lectures, by the Professor—Fee, £1 1s., daily at noon for the first three weeks of the Summer Session.

(*b*) Physical Chemistry, 40 lectures—Fee, £2 2s.

(*c*) Inorganic Chemistry, 40 lectures—Fee, £2 2s. (inclusive fee for (*b*) and (*c*) courses, £3 3s.), by Dr. Gray, extending over the last seven weeks of Summer Session (Mon., Wed., Frid., noon), and the following Winter Session (Mon., Tues., Thur., 3—4 p m. before Christmas, and Mon., Wed., Frid., noon, after Christmas).

(*d*) Advanced Physical Chemistry, 15 lectures, by the Professor—Fee, £1 1s., Thur. and Fri. at noon for the last seven weeks of the Summer Session.

(*e*) Organic Chemistry, 50 lectures, by Dr. Knox—Fee, £3 3s., Winter Session, Mon., Wed., and Fr. at noon before Christmas, and Tues. and Thur. at 3—4 p.m. after Christmas.

IV. *Chemical Laboratory.*—The Laboratory is open daily from 9 a.m. to 5 p.m. Each student on entering is allowed to arrange his hours of work so as to suit his own convenience, but must adhere to these hours when once fixed. The aim of the Laboratory Courses is to train the student in the practical methods of the science, so as to enable him to conduct chemical analysis and original research, and to apply chemistry to the arts and manufactures. Weekly Demonstrations, attendance on which is compulsory, are held in connection with the Laboratory Courses. (For further information as to fees and other conditions, see "University Fees").

Research.—The Laboratory is open for original work during both the Summer and Winter Sessions.

University of Aberdeen and Aberdeen and North of Scotland College of Agriculture.

Agricultural Chemistry and Forest Chemistry.

Professor—James Hendrick, B.Sc., F.I.C.

Assistant—(Vacant).

I. A Preparatory Course in General Chemistry including Organic Chemistry is given for those who are unable to take the full University Course. The course in Inorganic Chemistry consists of about sixty Lectures with Practical Work (seven hours weekly) during the Winter Session. The course deals with the general principles of Chemistry, and with those parts of Inorganic Chemistry which are of more immediate concern to students of Agricultural Chemistry. The Practical Work goes along with and illustrates the Lectures. Fee, £4 4s.

The course in Organic Chemistry consists of about thirty Lectures, and about thirty hours practical work, and is given during the Summer Session. It deals especially with those parts of the subject which are directly related to Agricultural Chemistry. Fee, £2 2s.

II. *Agricultural Chemistry* (*General Course*).—This class meets daily during the Winter Session, and three times a week during the Summer Session, and includes both Lectures and Laboratory Work. The Lectures deal with the Chemistry of the Atmosphere, the Soil, Manures, Foods, Preservatives, Insecticides, &c. The Physiological

Chemistry of Plants and Animals, the Composition and Manurial Requirements of Crops, and Dairy Chemistry are also treated of. The Laboratory Work is primarily intended to accompany and illustrate the Lectures. Exercises dealing with the properties and composition of Soils, Manures, Feeding-stuffs and Waters, and with the impurities and adulterations of these, occupy much of the time given to Practical Work. The fee for the whole Course (Lectures and Practical Work) is £4 4s.

III. *Forest Chemistry* (*General Course*) —Students in Forestry take the greater part of the General Lecture Course in Agricultural Chemistry, with special lectures on the Chemistry of Timber and Forest Products. The early part of the Laboratory Work is the same as in the case of Agricultural Students, but the later part is occupied with special exercises on Forest Products. Fee, £4 4s.

IV. *Laboratory*.—A Summer Course in Practical Chemistry is given to prepare students who have not previously done sufficient laboratory work for the course in Agricultural Chemistry or Forest Chemistry. Fee, £2 2s

V. The Laboratory is open daily from 9 a.m. to 5 p.m. for students who wish to study the principles and practice of Agricultural Chemistry or Forest Chemistry, or to undertake research in these subjects.

The fees mentioned above are subject to reduction in the case of students from counties and burghs within the College area, and there are a number of bursaries, some granted by local authorities and some by the University, open to students.

UNIVERSITY OF EDINBURGH.

Department of Chemistry.

Professor—James Walker, LL.D., D.Sc., Ph.D., F.R.S.

Lecturers—L. Dobbin, Ph.D.; A. C. Cumming, D.Sc.; J. E. Mackenzie, Ph.D., D.Sc.; S. A. Kay, D.Sc.; and H. G. Rule, B.Sc., Ph.D., and Demonstrators.

The three working terms are each of ten weeks' duration, viz.:—Autumn term, October to December; Spring term, January to March; Summer term, April to June.

Lecture Courses.—During the Winter Session a General Course of Chemistry for medical students is given. The class meets daily; fee, £4 4s. The First Course for Arts and Science students meets three times a week throughout the year; fee, £4 4s. The Second Course is given on Organic, Advanced Inorganic, and Physical Chemistry. The class meets three times a week throughout the year; fee, £4 4s. Tutorial Classes are held in connection with the First and Second Courses. All Arts and Science Classes are open to Women Students.

In addition to the above, Advanced Lecture Courses are given on particular branches of Physical, Organic, and Inorganic Chemistry.

Laboratories.—Practical classes for Medical Students meet during the Winter Session and in the Summer Session. (Fee, £3 3s.). The Elementary Laboratory course for Arts and Science students is held for four hours per week during the year. Fee, £4 4s. The advanced laboratories for Science and Arts Students engaged in analytical and advanced practical work are open daily from 9.30 till 4.30. Fees: Whole Day—Year, £16 16s.; one term, £6 6s. Half Day—Year, £8 8s.; one term £3 3s. Full Courses of instruction are given in Analytical, Practical Organic and Inorganic Chemistry (including Gas Analysis, Physico-chemical Measurements, and Assaying). Facilities are afforded to advanced students who desire to undertake chemical investigations.

Various prizes and scholarships are attached to the laboratory and general class.

Graduation.—Two Degrees in Pure Science are conferred, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.).

Candidates for Degrees in Science, if not graduates (by examination) in Arts in one of the Universities of the United Kingdom or in a Colonial or Foreign University recognised for the purpose by the University Court, must pass a preliminary examination in (1) English; (2) Latin, Greek, French, or German; (3) Mathematics; (4) One of the languages Latin, Greek, French, German, Italian, not already taken under (2), or Dynamics. In the case of a student whose native language is other than European, the Senatus may, at the Preliminary Examination, accept such language as a substitute for a modern European language. The Senatus may also in such a case accept as an alternative to Latin or Greek any other classical language, such as Sanscrit or Arabic.

The First B.Sc. Examination embraces Mathematics, or Biology (*i.e.*, Zoology and Botany), Natural Philosophy, and Chemistry. The Final B.Sc. Examination in Pure Science includes any three or more of the following subjects:—Mathematics, Natural Philosophy, Astronomy, Chemistry, Human Anatomy (including Anthropology), Physiology, Geology (including Mineralogy), Zoology (including Comparative Anatomy), and Botany (including Vegetable Physiology). In the Final Examination two written papers are set in each subject professed, the second of a higher standard than the first. Candidates must pass the first section in all, and the second section in at least one, of the subjects professed; the same regulations apply also to the Practical and Oral Examinations. Chemistry in this examination embraces Inorganic Chemistry, Organic Chemistry, and Physical Chemistry Practical Examination:—Complex Qualitative Analysis; Preparations; Gravimetric and Volumetric Analysis; Testing of Organic Substances. Each candidate taking the higher standard will also be examined on Ultimate Organic Analysis; Gas Analysis; Assaying; and Physico-chemical Measurements.

A candidate for the D.Sc. Degree must submit a thesis on original work done by him. The Thesis must be approved before the candidate is allowed to proceed to Examination. The candidate in Chemistry *may be* required to pass a searching examination in one of the following branches:—(1) The Chemistry and Chemical Technology of Inorganic Bodies, including Metallurgy; (2) Organic Chemistry; and to show a thorough practical acquaintance with chemical analysis in all its branches, and with the preparation of pure substances.

HERIOT-WATT COLLEGE, EDINBURGH.

Principal—A. P. Laurie, M.A., D.Sc., F.R.S.E.

Staff.—A. Archibald Buon, F.I.C., D.Sc., B.A. (Head of Department); Andrew King, M.A., F.I.C.; Clerk Ranken, D.Sc.

The curriculum of this College comprises both Day and Evening Classes, each department providing the higher general and technical education.

There is an extensive range of Chemistry Laboratories, embodying the most modern developments in laboratory design and equipment, and including a complete plant for the production of liquid air. The Chemistry Courses are designed to meet the requirements of Analytical and Technical Chemists. The College is a recognised training centre for the examinations of the Institute of Chemistry, and students can obtain the necessary instruction in General Chemistry, and also the specialised instruction required for the Final Examination for the Associateship of the Institute in the departments of Organic Chemistry, Metallurgy, Foods and Drugs, and Bio-chemistry.

The course for the Diploma of the College has been laid down on the same general lines as that required for the examinations of the Institute of Chemistry.

The Chemistry Courses are recognised by the University of Edinburgh as qualifying courses for the B Sc. degree.

Evening Classes are also provided in the subjects of Materia Medica and Botany.

A Laboratory, under the charge of Prof. Emil Westergaard, has been provided for the study of the Technical Mycology of Brewing, Distilling, Yeast Manufacture, Malting, Butter, Margarine, and Cheese Manufacture, Agriculture, Starch, Sugar, Preserve Making, &c. In this laboratory provision is made for the teaching of Biology, and the microscopic examination of Foods and Drugs, in connection with the examinations of the Institute of Chemistry.

Day Classes open on October 9th, and the Evening Classes on September 27th.

Matriculation Fee, 5s.; Composition Fees from £15 15s. to 21 guineas per annum. Full particulars are published in the Calendar of the College, which is issued early in September.

THE ROYAL TECHNICAL COLLEGE, GLASGOW.

Professor of Chemistry—G. G. Henderson, D.Sc., M.A., LL.D., F.R.S., F.I.C.

Professor of Technical Chemistry—T. Gray, D.Sc., Ph.D., F.I.C.

Lecturer on Dyeing—A. B. Steven, B.Sc.

Lecturer on Sugar Manufacture—T. H. P. Heriot, F.C S.

Professor of Metallurgy—A. Campion, F.I C., F.C.S.

Also, Professors and Lecturers in the other leading branches of Pure and Applied Science and Technology.

Session opens September 25th, 1917.

The main object of this College is to afford a suitable education to those who wish to qualify themselves for following an industrial profession or trade. It was founded by an Order in Council, dated November 26th, 1886, according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College (established 1796), the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments. The diploma course in Chemistry extends over four years.

Students who have matriculated at the University of Glasgow can qualify for the degree of B.Sc. in Applied Science by attendance on the Day Classes of the College.

Complete courses of instruction are provided in both Day and Evening Classes.

Copies of the Calendar for 1917-1918 may be had from the Director, Mr. H. F. Stockdale,; price by post, 1s. 4d. Prospectuses will be sent free.

UNIVERSITY OF ST. ANDREWS.

United College of St. Salvator and St. Leonard

Professor of Chemistry—James C. Irvine, Ph.D., D.Sc.

Reader in Organic Chemistry — W. N. Haworth, D.Sc., Ph.D.

Assistants—Geo. Robertson, M.A.; B Sc.; E. S. Steele, M.A., B.Sc.; Winifred Ross, M.A., B.Sc.; J. Anderson, M.A., B Sc.; J. Clarke, M.A

The Session begins on October 9th. A Competitive Examination, open to intending Students of Arts, Science, and Medicine, for about thirty-six Bursaries, ranging in value from £50 to £10 each per annum, is held annually in June. (For 1918 entries are due May 21s). One of these is open to Men or Women, and fifteen are restricted to Women, nine of the latter being intended for women who at the conclusion of their Arts or Science Course will proceed to Medicine. The remainder are open to men only.

A Hall of Residence is provided for Women Students.

Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), and Chemistry is also included in the curriculum for the M.A. Degree, and the M B., Ch.B. Degrees.; the regulations will be found in the "University Calendar."

Lecture Courses.

Three distinct Courses of Lectures are given, each extending over the three terms of the academic year.

First Year's Course.—This Class meets at 11 o'clock on five days in the week. The introductory lectures treat of the Nature of Chemical Action, the Classification of Substances into Elements and Compounds, the Phenomena of Oxidation, and the Composition of Air and Water. The Laws of Chemical Combination and the Atomic Theory are next discussed, after which the more commonly occurring elements and inorganic compounds are described systematically. Elementary Organic Chemistry is also included in the Course.

Special attention is given to those parts of the science which are of general educational value, and as much of the theory of chemistry is introduced as is compatible with elementary treatment.

This course of instruction is intended to meet the requirements of the M.A., First Science, and M.B., Ch.B. Exams., so far as Theoretical Chemistry is concerned.

Second Year's Course.—The first part of the Course is devoted to Organic Chemistry, and the second part to General and Physical Chemistry, the instruction in general being such as is required for the Final Science Exam. on the Lower Standard and the Special Exam for the M.A. Degree.

Third Year's Course.—Short courses of lectures on selected topics are given to Students preparing for the B.Sc. on the Higher Standard or the M.A. Degree with Honours.

Certificates are awarded on the results of examinations, and the "Forrester Prize" of about £10 is awarded to the best Student of the year.

Fee for the Session, for each Course, £4 4s.

Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., except on Saturdays, when it is closed at 1 p.m. The work pursued in the Laboratory comprises:—(1) The performance of experiments illustrative of the Principles of Inorganic and Organic Chemistry; (2) Qualitative and Quantitative Analysis; (3) Practical Physical Chemistry. Each student pursues an independent course of study under the supervision of the Professor or Demonstrator, the nature of the work varying with the proficiency of the student and the particular object he may have in view. Suitable courses of instruction in Practical Chemistry are provided for candidates for the Exams. in Arts, Science, and Medicine.

The fee for the Ordinary Course of Practical Chemistry is £3 3s, and for the Advanced Course £10 10s.

Original Research.

A special Research Department has been instituted by the University, the laboratories of which are open to students who give proof of their capacity to conduct original investigation. Graduates of other Universities who spend two years in the laboratory as Research Students are eligible for the D.Sc. degree of the University, and special chemicals and apparatus are provided free of charge. Graduate workers can also qualify for the Berry, 1851 Exhibition, and Carnegie Research Scholarships or Fellowships.

Students may work either independently or in collaboration with the Professor, to whom all communications should be addressed.

QUEEN'S UNIVERSITY, BELFAST.

Lecturer in Inorganic Chemistry—W. Wright, D.Sc., &c.

Lecturer in Organic Chemistry—A. K. Macbeth, D.Sc.

I.—*Chemistry.*—The lectures are delivered at 12 o'clock on the first five days of each week, and terminate about the end of March. The course embraces the elements of Physical, Inorganic, and Organic Chemistry. Fee, £3 3s.

II.—*Advanced Chemistry.*—Inorganic and Organic. The lectures are given at such days and hours as suit the convenience of the class. Fee, £2 2s.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of Qualitative and Quantitative Analysis, Inorganic preparations, &c. The class is held on four days in the week during the second term for two hours each day. Fee, £3 3s.

IV.—*Practical Chemistry for Engineering Students.*—A special course is given during the first term. Fee, £3 3s.

V.—*Laboratory Pupils.*—The Chemical Laboratories are open from the second week in October to the beginning of July, on the first five days of the week, from 10 a.m.—5 p.m. (except during the vacations). Students are admitted as working pupils on payment of a fee of £3 3s. for one term, £5 5s. for two, or £7 7s. for the whole Session. Facilities are provided for Students who wish to undertake research work.

Scholarships.—The following College Scholarships are awarded specially in connection with the schools of Chemistry and Physics:—Post Graduate Scholarships in Chemistry alone awarded annually of £50. and tenable for one year. Andrews Studentship in Chemistry and Physics, value about £73 annually, and tenable for two years. 1851 Exhibition Scholarships: One of these Scholarships has hitherto been placed at the disposal of the College every two years, of the annual value of £150, tenable for two or under special conditions for three years, and also one of the Industrial Bursaries.

UNIVERSITY COLLEGE, CORK.

A Constituent College of the National University of Ireland.

Professor—Augustus Edward Dixon, M.D.

Assistant Lecturer—John Taylor, M.Sc.

Demonstrator—H. R. S. Clo wo thy, B Sc.

The College Session will commence in October, 1917, and end in June, 1918. All classes are open to male and to female students.

The following courses are provided:—

1. First Year Course for B.Sc.—General and Elementary Physical Chemistry, Inorganic Chemistry, Introductory Organic Chemistry, Practical Chemistry.
2. Second Year Course for B.Sc.—Advanced Inorganic Chemistry, Advanced Organic Chemistry, Practical Chemistry.
3. Third Year Course for B.Sc.—Physical Chemistry, Advanced Organic Chemistry, Practical Chemistry.
4. Courses in Systematic and in Practical Chemistry for students of Medicine proceeding to the Degrees of the University, or to the Examinations of the Medical Licensing Bodies of Dublin and of Edinburgh.
5. Courses in Systematic and in Practical Chemistry for Students of Engineering.
6. Laboratory Practical Course for the Diploma in Public Health.

Full particulars as to Lectures, Fees, Scholarships, Exhibitions, &c., are contained in the Regulations extracted from the College Calendar, which will be supplied on application to the Registrar.

NATIONAL UNIVERSITY OF IRELAND.

University College, Galway.

Professor—Alfred Senier, Ph.D., M.D., D.Sc., F.I.C., F.C.S., M.R.I.A.

Demonstrators—Miss R. Clarke, B.A., D.Sc., and P. H. Gallagher, B.Sc.

The Session commences in September and ends in June.

Faculty of Science.—1. *First Year's Courses.*—Laboratory: Inorganic preparations, simple quantitative and simple qualitative determinations. Lectures: A study of the chief non-metallic elements, their reactions and compounds, the molecular and atomic hypotheses, the leading metals, and an elementary consideration of the constitution and reactions of typical hormathic and cyclic compounds. 2. *Second Year's Courses.*—Laboratory: Organic preparations, complex qualitative and quantitative inorganic determinations. Lectures: Advanced inorganic and organic chemistry. 3. *Third Year's Courses.*—Laboratory: Qualitative and quantitative organic determinations, molecular weight determinations, gas analysis, thermo-electro and photo chemical and other physical determinations. Lectures: General, physical, inorganic, and organic chemistry, a detailed study of special branches, and the historical development of chemistry.

Faculty of Arts.—*First Year's Course.*—Same as Faculty of Science.

Faculty of Medicine.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including the detection of the chief alkaloids, glucosides, and carbohydrates. Lectures: Same as in Faculty of Science, first year.

Faculty of Engineering.—*First Year's Courses.*—Laboratory: Same as in Faculty of Science, but less detailed, and including a special study of metals, alloys, and other materials used in building construction, also determination of hardness in waters. Lectures: Same as in the Faculty of Science, but not including organic chemistry.

The College offers a Scholarship in Chemistry for competition in alternate years of the value of £60, and Chemistry enters into the subjects required for numerous Scholarships in the Faculties of Science, Medicine, and Engineering. The Royal Commissioners for the Exhibition of 1851 offer every two years a Science Research Scholarship of £150 per annum. This Scholarship has already been held by six Chemistry Students of this College.

For details as to Fees, Regulations as to Scholarships, and other particulars apply to the Registrar, from whom the Calendar and other College publications may be obtained.

ROYAL COLLEGE OF SCIENCE, DUBLIN.

The Royal College of Science supplies, as far as practicable, a complete course of instruction in Science applicable to the Industrial Arts, and is intended also to aid in the instruction of teachers for the Schools of Science.

Diplomas are awarded in the Faculties of Engineering (Mechanical and Electrical), Applied Chemistry, and Agriculture. If accompanied by a certificate from the Professor of Chemistry, the Diploma of Associate of the Royal College of Science in the Faculty of Applied Chemistry is recognised by the Council of the Institute of Chemistry of Great Britain and Ireland as qualifying candidates for admission to the final practical examinations of the Institute.

The instruction in Chemical Science includes (1) General Inorganic Chemistry, Elementary and Advanced; (2) Organic Chemistry, Elementary and Advanced; (3) Analytical and Experimental Chemistry; (4) Physical Chemistry; (5) Metallurgical and Technological Chemistry and Assaying; (6) Instruction in Chemical Research.

Fees payable by Non-Associate Students:—£2 for each separate Course of Lectures. For Analytical Chemistry and Research—£5 for three months; £9 for six months; £12 for the entire session. Assaying—£5 for three months; £9 for six months. £12 for the entire session.

There are six Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for three years; two become vacant each year; they are awarded on the results of their examinations to Associate Students, not being Royal Exhibitioners, who have been a year in the College.

A limited number of Entrance Scholarships and Teacherships-in-Training in Science and Technology are competed for each year. These Scholarships are of the value of £50 a year for four years, and, in addition, entitle the holder to free instruction during the full Associateship Course.

For further particulars apply to the Registrar.

PROFESSIONAL CHEMICAL QUALIFICATION (F.I.C. AND A.I.C.).

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.—The Institute of Chemistry was founded in October, 1877, and incorporated by Royal Charter in June, 1885, to maintain the efficiency and integrity of the profession of Chemistry, including professional consulting and technological chemists, public analysts, and chemical advisers.

The Studentship. — Every Candidate for registration as a Student is required to produce evidence that he is at least seventeen years of age, and that he has passed a Preliminary Examination in subjects of general education, recognised by the Council of the Institute. He must also show that, at the time of making application for registration, he is working at a College or University recognised by the Council, or under the direction of a Fellow of the Institute in an approved laboratory.

The Intermediate Examination in General Theoretical and Practical Chemistry.—Candidates for admission to this Examination (Fee, £5 5s.) are required to produce evidence (I) of having passed an approved Preliminary Examination in subjects of general education; (II.) of having regularly attended systematic day courses, in a College or University recognised by the Council, during at least three academic years, in theoretical and practical Chemistry, and courses in Physics, Elementary Mathematics, and one of the following subjects, in accordance with the Regulations of the Institute: (i.) Higher Physics; (ii.) Advanced Mathematics; (iii.) Mechanics and Chemical Engineering; (iv.) Metallurgy; (v.) Geology and Mineralogy; (vi.) Physiology; (vii.) Bacteriology; (viii.) Agriculture; (ix.) Elementary Botany; (x.) Elementary Biology; and (III) of having satisfactorily passed the Class Examinations in all the subjects taken. As an alternative in the matter of training (II.), a candidate may take two years' day courses in a recognised Institution as indicated above, and work systematically for two other years under a Fellow of the Institute in an approved laboratory. A Candidate who has taken a Degree in Science (including Inorganic and Organic Chemistry, and Physics in the Degree Examination, Mathematics having been also taken at either the Final or Intermediate University Examination) in a University recognised by the Council, is eligible for admission to the Intermediate Examination of the Institute. Holders of certain Honours Degrees or Diplomas are exempt from passing the Intermediate Examination. A Candidate who has passed the Intermediate Examination of the Institute, or has been exempted therefrom is eligible for admission to the Final Examination.

The Final Examination (Fee, £5 5s.) *for the Associateship* (*A.I.C.*).—This comprises, in addition to a general knowledge of all branches of chemistry, a thorough knowledge of one branch—Mineral chemistry; metallurgical chemistry; physical chemistry; organic chemistry; chemistry (including microscopy) of food and drugs, fertilisers and feeding-stuffs, soils, and water; or biological chemistry. All Candidates for the Final Examination are required to translate French and German technological literature, with the aid of dictionaries. Candidates taking the food and drugs section must take a course in botany, and those taking biological chemistry a course in biology.

Fellowship (*F.I.C.*).—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practical work of applied chemistry in a manner satisfactory to the Council.

Full particulars are given in "The Book of Regulations for the Admission of Students, Associates, and Fellows," which may be obtained (gratis) from the Registrar, 30, Russell Square, London, W.C. Past Examination Papers, Annual Sets, 6d. each.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

CITY AND GUILDS OF LONDON INSTITUTE.—The Institute was founded in 1878, incorporated under the Companies Acts in 1880, and received the grant of a Roya Charter by Her late Majesty Queen Victoria in 1900. It is an association of the Corporation and Livery Companies of the City of London, instituted "for the purposes of all such branches of Science and the Fine Arts as benefit or are of use to, or may benefit or be of use to, productive and technical industries especially, and to commerce and industry generally or any branch thereof, and for the utilisation of such means as will promote the several exclusive purposes aforesaid" The operations of the Institute are divided broadly into four branches:—(1) The City and Guilds (Engineering) College, (2) the City and Guilds Technical College, Finsbury, (3) the City and Guilds South London Technical Art School, and (4) the Department of Technology of the Institute. *The City and Guilds (Engineering) College, Exhibition Road, S.W.*, forms the Engineering Section of the Imperial College of Science and Technology, and is conducted by a Delegacy representing the Imperial College, the City and Guilds of London Institute, and the Goldsmiths' Company. The College was included as a School of the University of London in the Faculty of Engineering in 1898. The courses of instruction cover a period of three years, and are in Civil and Mechanical Engineering, and in Electrical Engineering. They commence once a year in October, after the Matriculation or Entrance Examination of the College, and necessitate attendance through the Session. The age of admission is over 16 years. The fee for matriculated students attending a diploma course is £38 a session, if paid in advance. *The City and Guilds Technical College, Finsbury*, provides courses of instruction in Civil, Mechanical, and Electrical Engineering, and Applied Chemistry. The courses of instruction and the practical work in the laboratories and workshops are arranged solely with the object of providing a training on broad, practical, and scientific principles, in those matters which experience has shown best to fit a student to enter some one of the many careers connected with Civil, Mechanical, Electrical, or Chemical Industries or professions. The age of admission is 15 years. There is an entrance examination once a year, in September, and the fee for the Session is £20 if paid in advance. The object of the Institute's *Department of Technology, Exhibition Road, S.W.*, is the registration and inspection of classes in all branches of Technology, Domestic Subjects, and in Manual Training, and the holding of annual examinations in the subjects taught in such classes throughout the country and in the Colonies. The Programme of the Department, including regulations for registration and inspection, and for the award of Teachers' Certificates in Manual Training and Domestic Subjects, with Syllabus of Subjects, &c., published by Mr. John Murray, Albemarle Street, London, and is obtainable through any bookseller.

CITY OF LONDON COLLEGE, White Street, Moorfields.—A. W. Bain, B A., B.Sc., F.I.C., and Assistants. Classes and Laboratory Practice in Chemistry, open to Students of both sexes. Courses on Commercial Products—Milling (Flour), Tea, Textiles Session commences Oct. 1.

BATTERSEA POLYTECHNIC.—Principal, F. H. Newman, M.A., Ph.D. Inorganic, Organic, and Technological Chemistry, John Wilson, M.Sc. (Vict.), F.I.C. (Head of Chemical Department), and Assistants. Complete three or four years' day diploma courses of Instruction are given in Chemistry (Inorganic and Organic), together with Physics, Mathematics, Chemical Engineering and Engineering subjects, &c., for intending technological and works chemists. Certain of the Courses (Day and Evening) are recognised by the University of London in preparation for the B.Sc., for which examinations (Pass and

Honours) complete courses of instruction, under recognised teachers, are provided. Special Evening Courses (theoretical and practical) in various Technical subjects, as Fuel, Coal-tar Colours, Applied Bacteriology, Food and Drug Analysis, Pharmacy and Dispensing, Materia Medica, Paper Making and Testing, Oils and Fats. Special day and evening courses for the examination of the Institute of Chemistry, the Pharmaceutical Society, the Apothecaries' Hall, and the Conjoint Medical Board. For further information see the Polytechnic Calendar, an abridged copy of which may be obtained gratis from the Secretary of the Polytechnic.

Borough Polytechnic Institute, Borough Road S.E.—Chemistry Department under the Direction of C. Dorée, M A., D.Sc. Evening Lectures and Laboratory Work in Inorganic and Organic Chemistry. Special Lectures and Laboratory Courses in Electro-chemical Analysis, and the Chemistry and Technology of the Essential Oils. Special Courses of Lectures on various Technical subjects. (For further information see Institute Syllabus).

Birkbeck College, Breams Buildings, Chancery Lane. —Chemistry Courses conducted by G. Senter, D.Sc., Ph.D. (assisted by F. Barrow, M Sc., Ellen Field, MSc., Gwladys M. Lander, and A. Norah Kershaw), prepare for various Examinations, the B.Sc. and M.B. Degrees of the London University, Conjoint Board, Pharmaceutical Examinations, Board of Education, &c. The Session will commence on Monday, Sept. 24. The Day and Evening courses of study include Chemistry, Physics, Botany, Zoology, Geology, Mathematics, Latin, Greek, Modern Languages, Economics, Geography, Logic, History, and various branches of Law. All the Courses are conducted by recognised teachers of the University and provide for the Examinations of the University of London. The Calendar supplies detailed information respecting the Courses of Study, Examinations, &c.

Northern Polytechnic Institute, Holloway, London, N.—Principal, R. S. Clay, D.Sc. Instruction in theoretical and practical Inorganic and Organic Chemistry. Systematic Day and Evening Courses for the London University Degrees, Pass and Honours, also for the Board of Education examinations. Prospectus sent free on application to the Secretary.

Northampton Polytechnic Institute, St. John Street, E C.—Principal, R Mullineux Walmsley, D.Sc., &c. Day Courses in Electro-chemistry and Engineering Chemistry, and evening classes in Electro-chemistry, Electro-plating, Engineering Chemistry, Electro-metallurgy, Electrotyping, Stereotyping, and Metal Colouring. (For full details see Prospectus). Telephone, Holborn 1194.

South Western Polytechnic Institute, Manresa Road, Chelsea. — This Institute offers facilities for academic and technical education in many branches of Chemistry and Metallurgy. The department has designed both day and evening courses to meet the many requirements of these professions in London. Complete courses in General Chemistry, Metallurgy, and Assaying requisite for the B.Sc. and A I.C. Examinations, Technical Courses. Ample opportunity for individual work has been arranged for both day and evening students. A full list of these courses will be supplied on application. A feature of the laboratory work is the facility given for specialising in any particular branch of the above subjects, thus supplying a much needed want to men who have neither the time nor necessity for attending a degree course. The various lecturers will be pleased to advise intending students with regard to selection of courses. The department is under the control of J. B. Coleman, A.R.C.S., F.I.C., F.C.S., and the aim of the Institute is to make its courses of sound practical use to those engaged in Chemical Industries. Further particulars respecting the courses can be obtained from the Secretary (Room 79).

East London College, Mile End Road.—Chemistry: Professor, J. T. Hewitt, M.A., D.Sc., Ph.D., F.R.S.

Sir John Cass Technical Institute, Jewry Street, Aldgate.—Principal, Charles A. Keane, D.Sc., Ph.D., &c., assisted by R S Willows, M.A., D.Sc, H. J. S. Sand, D.Sc., Ph.D., G F. Morrell, B.Sc., Ph D., &c., Arthur R. Ling, F.I.C., C. O. Bannister, A.R.S.M, M.I.M.M., G Patchin A.R S.M., Arthur Harden, D.Sc., F.R S, &c., J. S. S. Brame, E. C. Snow, M.A., D.Sc., F. J. Harlow, B Sc., &c. The new Session of the Sir John Cass Technical Institute, which is especially devoted to technical training in Experimental Science and in the Artistic Crafts, will commence on Monday, Sept 24. The instruction in experimental Science provides systematic courses in Mathematics, Physics, and Chemistry for London University examinations in addition to the courses on higher technological instruction and on inorganic, organic, physical, and analytical chemistry, which form a special feature of the work of the Institute. The curriculum in connection with the Fermentation Industries includes courses of instruction on Brewing and Malting, and on the Microbiology of the Fermentation Industries. In the department of Physics and Mathematics, a special course of Lectures will be given on the Methods of Differential and Integral Calculus and on the Theory and Application of Mathematical Statistics, the latter of which will treat of the application of modern mathematical methods of dealing with statistical data in social, educational, economic, and physical problems. Opportunity will be given to students to investigate problems on their own account. In the Metallurgy department, in addition to the ordinary courses, special advanced courses are provided on Gold, silver, and allied metals, on Iron and Steel, on Metallography and Pyrometry, on Heat Treatment of Iron and Steel, and on the Mechanical Testing of Metals and Alloys. Full facilities are provided for advanced practical work and research in Chemistry, Metallurgy, and Physics.

East Ham Technical College.—Principal, W. H. Barker, B Sc. Head of Chemical Department—A. E. Dunstan, D Sc. (Lond.). Lecturers—F. B. Thole, D.Sc.; E D Griffiths, B Sc.; R. W. Wilson, F.C.S. Demonstrators—S. J. Plaice; A. G. Mossell. Chemical Engineering and Gas Engineering—A J. Nice. Gas Supply —G. Jenkins. Soap Manufacture—C. J. Benedict. Oils, Fats, and Waxes—A. J. Harvey. Tar Distillation, &c.— A J Nice and A. E. Dunstan, D Sc. Metallurgy—F. B. Thole, D.Sc. Sugar Manufacture—A. Wade. Painters' Oils, Colours, and Varnishes—R. A. Phillips. Evening Classes and Secondary School.

Blackburn Municipal Technical School.—Chemistry: Robert H. Pickard, D Sc. (Lond.), F.R.S, assisted by G. W. Clough, D.Sc., and L. Letter. M.Sc. Session commences Sept. 24. Full details of the Classes are given in the "Students' Handbook," which may be had at the Institution (price 1d., by post 3d).

Redruth School of Mines (now incorporated in the School of Metalliferous Mining, Cornwall).—Complete courses of Practical and Theoretical instruction are given in Inorganic Chemistry, Assaying, Mineralogy, Blowpipe Analysis, Mine Surveying, Geology, Principles of Mining, Ore Dressing, Mechanical Engineering &c., for intending Assayers, Mineral Chemists, Mining Engineers, and Surveyors. Practical instruction in Mining given at the School Mine. Syllabus on application.

Manchester School of Technology (University of Manchester.—The work of the School of Technology includes advanced study and research in various branches of science and technology, and undergraduate courses in the Faculty of Technology, extending over three years and leading to Degrees and Certificates in Mechanical Engineering, Electrical Engineering, Sanitary Engineering, Textile Industries, Printing and Photographic Technology, Architecture, and in the following branches of Applied

Chemistry :—General Chemical Technology, Chemistry of Textiles (Bleaching, Dyeing, Printing, and Finishing), Paper Manufacture, Metallurgy and Assaying, Fuels, Chemical Technology of Brewing, Electro-chemistry, Photography. The provision for the teaching of Chemistry is of an exceptionally complete character In addition to the laboratories for Inorganic and Organic Chemistry, Metallurgy, Brewing, Bleaching, Dyeing, and Electro-chemistry an extensive equipment (including machinery and appliances on an industrial scale) for demonstration, experiment, and original research in connection with the Bleaching, Dyeing, Printing, and Finishing, and Paper-making industries is provided in a separate building. A Brewhouse is also equipped on the low gravity principle with a plant of four bushel capacity.

TECHNICAL COLLEGE, SWANSEA.—Principal, W. M Varley, M.A., D.Sc., Ph D. Chemistry, E. A. Tyler M.A.; Metallurgy. H. I. Coe, M.Sc.; Physics, J. C. Kirkman, B.Sc. Day and Evening Courses in Pure and Applied Chemistry, Chemical Engineering, Metallurgy, and for Pharmaceutical, Medical, and Dental Students. Session opens Sept. 20th.

WOLVERHAMPTON MUNICIPAL SCIENCE AND TECHNICAL SCHOOL.—Principal, J D. Coales, D Sc., M.I.E.E ; Inorganic and Organic Chemistry, Th. J. Murray, M.Sc , Ph.D., and W. J. Lewis, B.Sc.; Physics, A. T. Harrison, B.Sc.; Botany, Mrs. Ashdown-Clarke, B.Sc. Human Physiology and Hygiene, H. J. Tench. Materia Medica and Pharmacy, F. W. Thompson, Ph.C. Day Classes in Chemistry, and Evening Classes in Chemistry Physics, Botany, French, &c. Special arrangements are made for the requirements of Pharmaceutical and Medical Students and Chemical Trades. Session commences Sept. 10th. For other particulars and programme, apply G. F Chell, Secretary.

MUNICIPAL TECHNICAL INSTITUTE, BELFAST.—Principal, F. C. Forth, F.R.C Sc.I. Chemistry, Prof. H Wren, M.A., Ph D., D.Sc. Day and Evening Courses.

REPORT OF THE COMMITTEE OF COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH.*

THIS is the Second Annual Report issued by the New Research Department, which under all the disadvantages of the strain of war and the shortage of workers is trying to provide a permanent basis for research in this country, and to co-operate with similar attempts in the Dominions.

The report indicates that there are three ways of organising industrial research. The simplest is the case where a single firm can work out a problem and itself fully exploit the results. In most cases, however, problems of industrial research will concern many firms—sometimes many industries; they will require the expenditure of large sums of money and the co-operation of many workers for long periods of time. But if successful the result will be of immense value.

Most individual firms cannot undertake this long and costly process. Yet why should the State pay for the whole cost of winning new knowledge which will be valuable to business men? It is hoped that the way out of this dilemma will be found by the establishment of "trade research associations," to be constituted as needed for each industry or group of industries, on which are to be represented when possible capital, management, science, and labour, and which are to be aided out of the million grant to be administered by the Department for the express purpose of establishing such research associations. One association is just about to be constituted for the cotton industry, others are being brought into existence for the wool, flax, shale oil, and photographic industries.

There are also many cases where the problem is so complex or else so immediately concerns the consumer rather than the producer that co-operation between manufacturing firms is not possible. This is obviously the case with fuel. Hence the establishment of the Fuel Research Board, which under the direction of a distinguished man of science. Sir George Beilby, will itself conduct research. So, too, with the problems of fire-resisting materials and the determination of standards and constants. All this is direct work for the whole community acting through its special organ of research. It is interesting in this connection that the Royal Society has recently negotiated with the Department the handing over of the financial responsibility for the conduct of the National Physical Laboratory, where investigations of national importance are constantly going on.

The main lines of policy of the new Department are being slowly worked out. But it is also not neglecting immediately pressing problems. In glass, for instance, a great deal has been already done—three completely new kinds of optical glass have been discovered by Prof. Jackson. A research on light alloys (aluminium, zinc, copper) will be of the utmost importance for the future of aeronautics. A new hard porcelain from purely British materials has already been produced. Researches into the recovery of tin are expected to save the Cornish tin industry £30,000 a year. A large number of other researches are being aided or carried out by the Department.

The Universities will take their place in the new social tissue whose pattern is now being woven. At a considerable number researches aided or initiated by the Department are now going on. At the Universities too the future research workers receive their training; and 36 (who would otherwise have drifted into immediately remunerative work) were aided by grants from the Department in 1916-17.

The report ends by noting the altered attitude of manufacturers and men of business towards the claims of research and education, and reiterates the conviction that a sure advance in industrial science can only be made when the field of work is adequately surveyed beforehand, and an organised plan of attack worked out.

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* To be purchased through any bookseller, or directly from H M. Stationary Office, Imperial House, Kingsway, price 3d , by post 4d

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxiv., No. 26, June 25, 1917.

New Method of Determining Aldehydic Sugars.—J. Bougault.—Aldehydic sugars, monoses or bioses, are oxidised by a mixture of iodine and carbonate of soda, giving the corresponding monobasic acid, the equation being $R.CHO + H_2O + 2I = R.CO_2H + 2HI$. The aldehydic sugars can be determined with great accuracy by measuring the amount of iodine they need for their oxidation. An accessory reaction accompanies this oxidation; it is due to the slow oxidation of the alcoholic functions of the molecule, and a correction can be applied for it. The ketonic sugars are not appreciably oxidised, and the aldehydic sugars can be determined in presence of them. The non reducing sugars behave like the aldehydic sugars. The chief drawback to the new method is the number of incompatibilities due to the mixture of iodine and sodium carbonate, which reacts with many organic compounds.

Vol. clxv., No. 1, July 2, 1917.

New Method of Destroying Tissues for the Estimation of Arsenic, and the Examination of Ash.—Armand Gautier and P. Clausmann.—The usual method of destruction of tissues for the estimation of arsenic, although very safe when absolutely pure reagents are used, suffers from some disadvantages. It is very laborious and delicate, and requires large quantities of acids which are not easy to obtain in the pure state. The new method is accurate, simple, and quick. The animal or vegetable matter to be examined is heated to 300° and then powdered. It is mixed with 2 or 3 per cent of its weight of quicklime, and a little water is added. The mixture is then heated to a low red heat in a muffle furnace, and after cooling the ash is powdered and taken up with water. A few drops of sulphuric acid are added, and the liquid is boiled, filtered, and concentrated until white fumes are given off. The acid liquid is then diluted with 8 to 10 volumes of water, and transferred to Marsh's apparatus. Arsenic can be detected within eight hours by this method, while the usual method requires three days. The method has also been found to be very accurate.

Acid Sulphate of Zirconyl.—Ed. Chauvenet.—By cryoscopic methods the author has found that the most stable state of the system SO_3 and ZrO_2 is $\left[Zr<^{O}_{SO_4} . ZrO_2\right]$. The compounds of the zirconyl radical have a strong tendency to form compounds of the type $Zr<^{O}_{A} . ZrO_2$, where A is an acid radical.

Determination of Free Chlorine in Solutions of Hypochlorite.—F. Dienert and F. Wandenbulke.—In Penot's method free chlorine is determined in presence of hypochlorite by titrating with arsenious acid and iodine. The method is rendered more sensitive by adding a large excess of an ammonium salt and potassium iodide; this prevents the formation of iodate, and the chlorine can thus be determined directly in an alkaline medium by arsenious acid. Dilute solutions of hypochlorite have always to be used.

No. 2, July 9, 1917.

Influence of Mineral Matter upon the Germination of Peas.—L. Maquenne and E. Demoussy.—Peas were grown in sand to which was added distilled water containing known amounts of metallic salts, and the roots were measured after germination had been allowed to proceed for six days. Calcium appears to be the only substance which, in absence of all others, is capable of producing normal germination. Exceedingly small quantities produce the effect, usually smaller than those necessary for toxic substances to act. After calcium come strontium, manganese, aluminium, barium, and magnesium, which are much less favourable; then the alkaline metals and zinc, lead, and copper, which seem to have no immediate effect. The study of the growth of the stem in similar conditions will be the subject of a further investigation.

MISCELLANEOUS

County of Northumberland Agricultural Station.—The work of the County of Northumberland Agricultural Station at Cockle Park is being continued with valuable results, as shown by the Report for 1917 recently issued by the Director, Prof. Douglas A. Gilchrist. The Report contains details of the manurial and rotation experiments, the bulletins of feeding experiments being published separately. The results are of special interest to the Northumberland agriculturist, and the Reports of the experiments can be obtained on application to the Secretary of the Northumberland Education Committee, The Moothall, Newcastle-upon-Tyne.

Literary Intelligence.—Messrs. J. and A. Churchill will shortly publish "A Short Account of Explosives," by A. Marshall, A.C.G.I., F.I.C., Chemical Inspector, Indian Ordnance Department. The book is dedicated, by permission, to Field-Marshall Sir Douglas Haig, K.T., &c. It gives a clear and simple account of the main facts concerning explosives and their properties. There are 29 illustrations. Also "Allen's Commercial Organic Analysis," Vol. IX., edited by W. A. Davis, B.Sc., A.C.G.I. This volume contains articles by about thirty contributors, bringing the preceding eight volumes up to date, and indices covering the complete work

INSTITUTE of CHEMISTRY
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Forms of application can be obtained from The Registrar, Institute of Chemistry, 30, Russell Square, London, W.C. 1.

Regulations for the Admission of Students, Associates, and Fellows. Gratis.
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PHARMACY and DISPENSING. Wednesday and Thursday. R E. Griffiths, B Sc., F.I.C.
DRUG ASSAY and MATERIA MEDICA. — Wednesday and Thursday. R. E. Griffiths, B.Sc., F.I.C.
OILS and FATS.—Monday. J. L. White, D.Sc.
PAPER MAKING. — Monday. D. R. Davey.
PAPER TESTING. Friday D. R. Davey.

Next SESSION begins on MONDAY OCTOBER 1st, 1917.
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Fees and full particulars may be obtained from the Secretary Room 79). Telephone 899 Western.

THE CHEMICAL NEWS

Vol. CXVI., No. 3016.

THE UTILISATION OF THE SULPHUR CONTENTS OF ZINC ORE.*

By H. M. RIDGE.

SPELTER was formerly made only from calamine, or zinc carbonate, but as the world's supply of this mineral is limited it became necessary, particularly about the middle of the last century, to use zinc sulphide ore, and the demand increased very rapidly.

The main source of spelter to-day is zinc blende. When pure this consists of zinc sulphide with 67 per cent of zinc and 33 per cent of sulphur, and is a white transparent mineral. The pure mineral is rarely found; zinc blende is generally black or brown, and contains several per cent of iron as amorphous FeS, and frequently also some manganese. In consequence of impurities the sulphur content is usually less than the above mentioned figure, but if pyrites, FeS_2, is present the sulphur assay rises.

In the ore deposits zinc blende is usually associated with galena, and occasionally with copper pyrites, but it is found with most sulphide ores. No particular kind of gangue predominates; in addition to quartz, calcite, strontianite, magnesite, ankerite, siderite, barytes, and fluorspar are frequently present. Quartz and calcite are lighter than blende, barytes is heavier; the differences in specific gravity are sufficient to allow of separation by ordinary wet methods of concentration. If fluorspar is present wet concentration should be carried out carefully, because it is desirable to remove fluorine as far as possible. Siderite and ankerite have been taken out efficiently on the Continent on magnetic separators after a preliminary flask roast to form magnetic Fe_3O_4.

The utilisation of the zinc contents of the big deposit of argentiferous zinc and lead ore at Broken Hill presented unusual difficulty, because of the presence of garnet and rhodonite of about the same specific gravity as zinc blende. This was first overcome by the use of the Wetherill electro-magnetic separator with an intensely strong magnetic field. When the author started the first of these plants at Broken Hill in 1899, the garnet and rhodonite were lifted out of the ore with one set of machines, and then the residue was passed through an even stronger field which separated the zinc blende from the galena, quartz, and calcite. The process was too expensive to be able to compete permanently, and was superseded by the modern methods of flotation. Unfortunately, flotation methods are not, up till now, effective for separating fluorspar or carbonates from blende.

The rapidly increasing consumption of spelter threatened to cause a shortage of ore as long as calamine was the main source of supply, but improved methods of concentration and of smelting have resulted in making available enormous resources of sulphide ore, and there is an adequate supply of suitable concentrates to cope easily with all prospective demands.

The Extraction of the Sulphur from the Mineral.

The sulphur can be separated from the zinc by (*a*) smelting with a metal having a greater affinity for sulphur; (*b*) treatment with the oxide of a strong base; (*c*) heating in the presence of oxygen.

Zinc sulphide is decomposed by molten metallic iron or copper, and a sulphide is formed, while metallic zinc vapour is driven off. Considerable experimental work has been done on this process, but without success, because of the expense of wasting the iron or copper sulphide, and the possibility when copper is used of losing some of this metal in the process. The operation has to be carried out in a retort or crucible at a high temperature. This has some similarity to the ancient methods of brass manufacture by smelting copper ore and zinc carbonate together with carbon.

Zinc blende can be smelted with lime and carbon to form zinc, carbon monoxide, and calcium sulphide; this has been carried out in an electric furnace, but it entails a continuous fresh supply of lime, while the resulting impure sulphide of lime quickly oxidises to sulphate, and has to be run to waste.

The usual method of separating the sulphur from blende is to roast the ore with a sufficiency of air to form zinc oxide and sulphur dioxide. This is the method in general use.

The further treatment of the zinc concentrates after roasting consists in heating the zinc oxide in retorts, with suitable reduction material, to reduce the oxide and distil the reduced metallic zinc which is cooled and condensed to liquid metal.

In roasting zinc blende the sulphur is oxidised to SO_2 with a small amount of SO_3, and sufficient oxygen is required for the formation of zinc oxide. The reaction is exothermic, but it is not possible to obtain a sweet roast without the application of heat. Sulphates are formed in roasting, and these have to be decomposed; this necessitates additional heat units. The heats of formation are:—

$Zn+S$ .. .. .. = 43,000
$Zn+O$ .. .. .. = 84,800
$2S+O$ .. .. .. = 69,260

If 97 kgrms. of zinc sulphide are oxidised completely with air containing 48 kgrms. of oxygen, 81 kgrms. of zinc oxide, and 64 kgrms. of sulphur dioxide, equal to 22·22 cub. m. are obtained. 208 kgrms. of air with 160 kgrms. of nitrogen will be used. The reaction gives:—

Formation of 81 kgrms. ZnS ..	+84,800	calories
" 64 kgrms. SO_2 ..	+69,260	"
Total	154,060	"
Decomposition of 97 kgrms. ZnS	−43,000	"
Net heat evolution	111,060	"

In practice this result is not obtainable; the ore and the air have to be heated up, while the wasted ore and the sulphur fumes are discharged at a high temperature, and as the heat units cannot all be retained in the furnace, coal has to be burnt to maintain the temperature and to remove the last units of sulphur.

If the sulphur has to be used for technical purposes the fumes must not be contaminated and diluted with fire gases. Constructional difficulties were encountered in the design of furnaces for this purpose. Muffled furnaces have to be used in which the fire gases do not come into contact with the ore, and the heat units have to be passed through fire brick in order to maintain the heat while the last units of sulphur are being oxidised, and while any sulphates, which may have been formed, are decomposed.

In Germany and Belgium prolonged efforts were made to prevent the emission of large quantities of sulphur fumes into the air, and the consequent destruction of vegetation in the neighbourhood of the works, and the first practical results were obtained about 1855 by Hasenclever, who, after a series of experiments, built a furnace at the Rhenania works. This furnace has two roasting hearths of which only the top hearth is muffled, and after the ore has been rabbled along this hearth and has given off some of its sulphur, it is dropped to the bottom hearth to complete the roasting in direct contact with the fire gases. The arches of the furnace were too high for practical work, and the fumes were low in SO_2. In 1865 an improved furnace was built, but its capacity was small and the strength of the gas continued deficient; it is worthy of note that the designer realised that it was only necessary to heat the ore during the last stages of oxidation, because there is enough heat at the commencement of roasting, but this point was overlooked for many years. The general idea of the construction of the furnace is very similar to that of "Delplace," which will be referred to later.

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* Abridged from a Paper published in the *Journal of the Society of Chemical Industry*, xxxvi., No. 13.

An effort to reduce the amount of labour was made in 1872 with a furnace which, however, laboured under the disadvantage of the final roast being carried out in contact with the fire gases. The furnace had 215 square feet of area on the bottom direct fixed hearth and above this a muffle of the same size was heated above and below by the fire gases. The ore passed down an incline of 43°, and baffles were placed in this so as to spread the ore in a fairly uniform thin layer. Openings were arranged for access in case of blockage. The ore travelled a total distance of about 90 feet in the furnace. Much labour was required for breaking up lumps of ore which formed, and the furnace had to be very carefully tended. During the period when much sulphur is being given off the ore will run like water if the temperature rises too high, and if iron or lead are present in appreciable quantity the overheated ore will set hard. This frequently occurred in the incline, and the design was finally discarded because more labour was required for freeing the incline than is necessary for working a horizontal hearth. The output of the furnace per twenty-four hours was about 3 tons of roasted ore with a coal consumption of 15 cwt., and three men were necessary per shift, so that the output per man per shift was only 10 cwt.

In the furnaces which were designed for part of the work to be done in the muffle and the balance in a reverberatory, only about two-thirds of the sulphur contents were available for further use, while the remaining one-third was so diluted by the fire gases that it had to be allowed to escape into the atmosphere.

In England attempts were also made to roast zinc ore in muffle furnaces, but they were not entirely satisfactory. It is remarkable that the first roasting of blende appears to have been done here. In 1758 John Champion, of Bristol, obtained a patent for using blende or black-jack in the manufacture of brass.

The first of the furnaces of the so-called Rhenania type was built in accordance with a German patent of 1882. The furnace is provided with one fire-box, and the fire gases travel four times the length of the furnace, which has nine muffles each 2 ft. 5½ in. wide, and four hearths in which the ore is rabbled by hand at right angles to the direction of the travel of the fire gases. The air for the muffles is preheated, and the sulphur fumes leave the furnace with about 6 per cent SO_2. The capacity is 3 to 3½ tons of roasted ore with a coal consumption of 27 per cent; the ore remains in the furnace about forty-eight hours. Improvements were made in this furnace by cutting out the division walls between the muffles, so that the ore could be rabbled sideways along the hearths in the opposite direction to the travel of the fire gases; later, it was found unnecessary to heat the upper parts of the furnace because the oxidation of the ore gives off sufficient heat, but before this stage was reached furnaces were built embodying almost every conceivable variation in the arrangement of the fire flues and the muffles.

One of the later modifications of the Rhenania furnaces is 47½ ft. long by 17½ ft. wide, and the ore travels a distance of 118 ft. along the hearths. With a twelve-hour shift a total of eight men was required for the production of 6 tons of roasted ore per twenty-four hours. By working with eight-hour shifts only six men were required, and the production per man per shift rose from 14 or 15 cwt. to 18 or 19 cwt. The coal consumption is about 25 per cent.

These furnaces have generally been built together in blocks of four, and have been more largely used than any other type.

Owing to the high price of fuel, since 1895, "Delplace" furnaces have been largely built in Belgium. This furnace has seven superimposed hearths, in which the travel of the ore is only 40 ft., but it is exposed thoroughly to the air because the arches are low, and only a thin bed of ore is maintained on each hearth. Only 16 per cent of coal is required for heating. These furnaces have been built mainly in Belgium and in France, but a few have also been erected in this country and in Germany. Experienced labour is required to work them satisfactorily, and the men prefer to work on the Rhenania furnaces in which the ore is rabbled sideways, whereas in the Delplace type it has to be alternately pushed from and drawn towards the worker.

Work on zinc ore-roasting furnaces is most laborious, and even on the Continent continuous efforts have been made, ever since the start of the industry, to replace hand labour by machinery. The first attempt to do this was made by the Société de la Vieille Montagne, who succeeded in carrying out the first part of the operation in a furnace like a MacDougall burner for pyrites, but although various modifications of this furnace were tried it was not much used, mainly because of mechanical difficulties, which forty years ago proved insuperable.

In America, where hand labour was even more difficult to obtain, it was impossible to use hand furnaces. Hammond and Spence designed a furnace which was the forerunner of the Hegeler furnace, now largely used in the United States. This furnace occupies a very large floor area; it treats 40 tons per day with a coal consumption of about 25 to 30 per cent. It contains seven superimposed hearths over which ploughs are drawn by chains, passing first through the furnace in one direction and then being moved to the level of the next hearth, and passing over this in the opposite direction. This allows of cooling the stirring mechanism outside the furnace. The capital outlay is large, and it is said that the repair bill of the furnaces working on the Continent is such that there is no appreciable saving in cost of roasting as compared with hand-rabbled furnaces. With eight-hour shifts seventeen men are required per shift, so that there is no reduction in the number of men as against hand furnaces, but the men can mostly be ordinary unskilled labour together with a few mechanics.

Great things were expected of the "Meston" furnace, a number of which were built in Tasmania, but have been found unsatisfactory, not being strong enough for the work. The Wedge furnace is now being tried on zinc ore in America, while the Spirlet furnace was at work in Belgium and Germany at the outbreak of the war, and some have also been built in America. The capacity of the furnace is 3 to 3½ tons per twenty-four hours, and in consequence of there being no metal parts inside the furnace in contact with the ore the fuel consumption is low. The alternate hearths rotate, and the ore is stirred by means of special bricks projecting downwards from the hearth above. Good results have been obtained, but the campaign is short, and as soon as one or two of the projecting bricks, which stir the ore, wear or break off the furnace chokes and has to be cooled down and put out of commission. On the Continent it has only been possible to work a furnace continuously for a maximum of three months before the arches have to be removed and overhauled, because no repairs can be carried out while the furnace is working.

In the Ridge mechanical zinc blende furnace the mechanical arrangements have been so far worked out that freedom from mechanical difficulties is assured while the whole furnace is accessible. The shafts are each made in one piece and are water-cooled; about 15,000 gallons of cooling water are passed through the shafts in twenty-four hours to prevent overheating. The rabbles which stir the ore are easily and quickly renewed, and the part to be replaced weighs only 5 lbs. The ore is fed continuously to the drying hearth on top of the furnace, and passes down over three roasting hearths and finally to the cooling hearth, where it serves to preheat the air required for the oxidation. The mechanism of each furnace is driven by a separate electric motor which takes 8 to 10 horse-power. The motor and all the gearing are on a solid foundation beneath the furnace and fully accessible. The discharge opening is separated from the gearing by a brick wall to keep out all dust. The furnace is noiseless, the only sound being the hum of the motor. It is gas-fired, and the gas is burnt only under the bottom roasting hearth. Broken Hill zinc concentrates are roasted down to 0·75 per cent total sulphur with a feed of 12 tons of ore per day of twenty-four hours and a coal consumption of 10 per cent. The sulphur fumes leave the furnace with 6½ to 8¼ per cent sulphur dioxide, and at a temperature of 380° C. so that they can be used satisfactorily in the lead chamber process. One man per shift can attend to the furnace and the producer.

Zinc concentrates with 14 per cent lead have been satisfactorily treated, and also concentrates with 17 per cent iron; when roasting an ore high in lead or iron it is essential that a mechanical furnace be kept working continuously, because half an hours' stoppage means that the ore on the hearths sets hard, and forms lumps which have to be broken up. It has been found possible in this furnace to use the rabbles for breaking up the lumps, and the gearing can, if necessary, be run alternately backwards and forwards till the hearths are free.

In some ores the presence of substances which interfere with the desulphurising is important; lime, magnesia, strontia, and baryta, if combined with sulphur, retain it in the roasting furnace; if combined with carbonic acid this is driven off, and in some cases the lime, &c., will take up sulphur from the ore. In considering the sulphur contents of roasted blende allowance must be made for this combined sulphur. Lead becomes a nuisance in hand-rabbled furnaces, but causes no trouble in a properly designed mechanical furnace; if ore high in lead is treated continually an accretion will form on the hearths, but the rabbles can be made to remove this. High iron content is found in some Spanish and German ores, and makes complete roasting in hand furnaces almost impossible. In Germany the author was able in a mechanical furnace to reduce the sulphur left in the roasted ore to more than 1 per cent less than had been possible in hand furnaces.

The Utilisation of the Sulphur. Statistics and Economics.

The sulphur dioxide given off in roasting is utilised for making sulphites, liquid SO_2, or sulphuric acid.

Aluminium sulphate has been made at Flone, in Belgium, by passing the roasted gases into large chambers excavated on the hill-side, and filled with alum shale. At Ampsin this method was also used for making alum with gas from reverberatory furnaces; it seems that sulphite is formed, and this readily oxidises to sulphate.

The manufacture of liquid SO_2 was started by Grillo at Hamborn, in Westphalia, because the fumes from the roasting furnaces were low in SO_2, and it was at that time considered impossible to utilise them for making sulphuric acid. The furnace gases pass to a scrubbing tower sprayed with water which dissolves the sulphur dioxide, and the liquid gravitates to a series of pans, which are placed over the burners, the heat of which is sufficient to drive off the SO_2 gas which, after being cooled, is compressed and liquefied at a pressure of 7 atmos. In Germany two plants are in operation, viz., one at Hamborn and another at Lipine, in Silesia, but in this country the method has not been employed on the fumes from zinc ore. The demand for liquid SO_2 is limited.

The main commercial use for the sulphur fumes is the manufacture of sulphuric acid, and this can be carried out in lead chambers or by the contact process.

Most zinc ores offer the advantage of being free from arsenic, but, on the other hand, they frequently contain fluorine, of which even as little as 0·01 to 0·02 per cent becomes noticeable. Fluorine occurs with the ore as calcium fluoride, which is decomposed in the roasting furnace in the presence of silica and forms silicon fluoride. If this gas passes into the Glover tower it is decomposed and hydrofluosilicic acid is formed; this, in turn, appears to be split up. As it is usual, when treating zinc ores to circulate the tower acids, the fluorine contents seem to remain in the circuit so that the attack on the packing of the towers gradually increases, but contrary to expectation the author has not found increased corrosion of the lead work of the chambers by fluorine. Many efforts have been made to overcome the trouble with the packing. Glover towers have been built entirely of lead, and with lead sheets as a packing so as to avoid the use of silicious material, but it is found necessary in this case to use two Glover towers in series, the first one being an empty tower followed by a tower filled with suspended lead sheets. The author has found it preferable to overcome the trouble by passing the whole of the chamber acid through the towers instead of only circulating the tower acids, and by this means keeping down the fluorine contents of the acid, and at the same time to pack the towers with a well-burnt brick packing of a suitable composition which would offer the maximum possible resistance to the attack of hydrofluoric acid. Glover towers built in this way and properly operated have been worked continuously for twelve months and longer without trouble.

Mercury is found in some Spanish blendes. It collects at the outer part of the dish of the lead chamber, where it is not protected by lead sulphate, and causes rapid corrosion of the lead. This can be overcome by lining the sides of the dish with thin brickwork.

Antimony occurs frequently in small quantities with zinc blende, and at the high temperature of the roasting furnace some of this is volatilised and passes into the acid. Antimony was found in the zinc concentrates from Broken Hill when treating ore from the upper levels in one of the mines, but the quantity present was less than 0·03 per cent.

Most zinc ores have lead associated with them, and some of this is generally driven off with the sulphur in the roasting furnace together with the silver which is combined with the lead, but both the lead and the silver are deposited in the chamber sludge.

The lead chamber process, when working with hand furnaces, has to be carefully watched because of the intermittent evolution of sulphur dioxide in consequence of intermittent rabbling of the ore. In Germany it has been usual to reduce this difficulty by arranging for the furnace hands, working on different furnaces, to start their shifts at different times, but in spite of this it is not possible to obtain a continuous current of uniform gas throughout the twenty-four hours, and unless the process is watched carefully loss of nitre is the result. With modern mechanical furnaces this trouble does not occur.

The design of the chamber plant does not call for special comment. It is in every way similar to that used when burning pyrites. The nitre consumption and working cost of the plant are not higher than with pyrites.

Here and in Belgium lead chamber plants have been used exclusively for making acid, and in Germany this is also the rule, but there are several contact acid plants at work as well. In America fourteen zinc smelters make sulphuric acid, but they mainly use the contact process.

Calculated as 60° B. acid the American production from zinc blende was:—

In 1911	230,643	short tons
„ 1912	292,917	„
„ 1913	296,218	„
„ 1914	411,911	„
„ 1915	484,942	„

The average price realised in 1915 was 8.85 dols. per short ton.

The use of the contact process for fumes from zinc ore made the biggest strides in the United States, because there the smelters are largely able to rely for their ore supplies upon the produce of one or more mines, and are not dependent upon small parcels of ore shipped from various parts of the world, as has been the case here and there on the Continent. They have, consequently, been able to make provision for eliminating any harmful ingredients which may be present in the raw material which they expected to be treating over a long period. The American smelters also have the advantage of having practically no hand-rabbled furnaces.

The various contact poisons can be eliminated if the tonnage to be treated warrants the initial expenditure on the plant. Fluorine, arsenic, antimony, and lead can be removed by first scrubbing the gas with a suitable liquid, and when this is done the conversion offers no greater difficulties than when brimstone or pyrites is burnt.

In England acid has only been made from zinc ore in three plants, and their estimated tonnage does not exceed 25,000 tons a year of 140° Tw. acid. This tonnage corresponds to a production of about 10,000 tons of spelter. In 1913 31,290 tons of virgin spelter were made in the country. Part of this was made from calamine, but the available supplies of this ore are steadily decreasing, and it is only a question of a short time when the whole of the metal will have to be smelted from zinc blende. The position is really worse than is indicated by these figures because it has been customary to roast the sulphide ore in reverberatory furnaces from which the fumes cannot be used, so that the sulphur is wasted and the atmosphere polluted.

To illustrate the importance of the utilisation of the sulphur of zinc ores the figures for Upper Silesia are given below. The district produces about 60 per cent of the spelter made in Germany, but a good deal of calamine is still available there, so that the maximum production of sulphuric acid from blende has not been reached; the tonnage of calamine treated steadily decreases, but the increased amount of blende compensates for this, and allows of an increasing spelter and acid production. The last figures available are for 1911, and the table shows the results for every fourth year from 1887.

Statistics from Upper Silesia.

Year.	Raw blende washed. Metric tons.	Sulphuric acid reduced to 50° B. Metric tons.	Sale value.	
			Total (marks).	Metric ton of 50° B. acid (marks).
1887	53,882	21,013	479,000	22.81
1891	66,236	32,676	746,000	22.85
1895	84,857	33,229	778,000	23.43
1899	123,602	64,029	1,074,000	16.77
1903	187,596	104,268	1,728,000	16.62
1907	421,006	139,840	2,187,000	15.65
1911	411,352	213,317	3,025,000	14.18
1912	—	254,008	—	—

Six works still used their old reverberatory furnaces so that not all the sulphur could be utilised, but for some years factory legislation has prohibited the emission of noxious fumes, and as the plants become worn out they have to be replaced by modern installations. The fumes from the reverberatory furnaces are scrubbed with milk of lime which is sent to waste. Five plants have lead chambers, and make acid of 50°—55° B.; this is generally concentrated in cascades or Kessler apparatus, and in recent years largely in Gaillard towers. Three works have contact plants as well as lead chambers. There was in 1912 a total of 48 lead chambers.

Of the total production of acid:—41,055 metric tons were sold as acid of 50° B.; 114,346 metric tons were sold as acid of 50°—60° B.; 42,349 metric tons were sold as acid with 98—100 per cent H_2SO_4; 216 metric tons were sold as oleum with 20 per cent SO_3; 4774 metric tons were sold as SO_3; and in addition 2855 metric tons of liquid SO_2 were made.

The acid is used for making superphosphates, sulphate of ammonia, dynamite, and gun-cotton, and for refining mineral oil. It is distributed by rail over a wide area, some going into Russian-Poland, Austria, Hungary, and even to Roumania.

The position in the zinc smelting districts in Western Germany is analogous, but the make of acid there is larger in proportion to the production of spelter, because there is no local supply of calamine. The newer smelting works have been placed on navigable water-ways so that freights on raw materials and finished products are low. The chamber process is used in all the works except one which has a contact plant; there is also one installation making liquid SO_2.

In 1913, in Germany, 554,760 metric tons of blende were roasted for making sulphuric acid; of this 87,439 tons were imported from Australia and 56,181 tons from other countries.

In Belgium blende is mainly roasted by the chemical manufacturers, who retain the sulphur and receive from the zinc smelter in addition a payment of 6 to 8 francs per 1000 kgrms. for roasting the ore. This was facilitated by the low freights on the canals, which reduced transit charges to a very low figure. In Belgium 65 per cent of the total production of sulphuric acid is made from blende; the amount of zinc is nearly 400,000 tons.

The most important and serious factor for consideration here in England is the shortage of zinc smelting capacity in the country. In 1913 our consumption of spelter amounted to no less than 224,000 tons, of which 74 per cent was imported. After allowing for the metal made by the refiners we imported about 166,000 tons of spelter and zinc in other forms. If this quantity were all made from blende the roasting fumes could be used to produce annually 400,000 tons of 140° Tw. acid. There is no reason why this should not be done, and the corresponding quantity of brimstone and non-cupreous pyrites displaced as well as a portion of the pyrites which is low in copper.

Before the war the cost of making 140° Tw. acid from zinc ore fumes in this country was only between 8s. and 9s. per ton, so that the operation is remunerative and profitable.

Zinc ore must be treated because spelter is required, and if the work is not done here it will be done elsewhere. Cheap sulphuric acid has always been an important factor in the chemical industries, and unless we use the resources of the Empire others will do it for us, and we shall be obliged to continue to look on while the foreign subsidiary industries using the acid abroad go ahead.

WAVE-LENGTHS OF THE STRONGER LINES IN THE HELIUM SPECTRUM.*

By PAUL W. MERRILL.

I. *Introduction.*

For both practical and theoretical reasons the spectrum of helium is of considerable importance in spectroscopy and related branches of science. It consists of a comparatively small number of lines well distributed from the ultra-violet to the red, and is conveniently produced in great intensity in an ordinary vacuum tube. Hence it is widely used as a reference spectrum in spectroscopic and optical work of many kinds, but the wave-lengths have not been known with sufficient accuracy for the most precise wave-length measurements. It is thought that the present determinations will supply this deficiency and make possible the use of helium lines as standards of wave-length. This investigation is a part of the standard wave-length programme of the Bureau of Standards, which has been under way for two years, and which is at present chiefly concerned with the spectra of iron, argon, and neon.

Helium is of great interest in astronomical observations as it is one of the most important elements from a cosmic viewpoint, its spectral lines being prominently observed in such radically different objects as nebulæ, early—that is, blue or white—stars and the sun (flash spectrum).

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* *Bulletin 302 of the U.S. Bureau of Standards*, 1917.

As an aid to progress in the comprehension of the structure of matter nothing is of greater promise than an accumulation of accurate data in regard to spectral-line series. Thanks to the early investigations of Runge and Paschen, every line observed in the ordinary spectrum of helium may be placed in one of six series. In order to establish the mathematical form of these series and to throw light on their relations to one another as well as to the series of other elements, exact values of the wave-lengths of numerous lines will be required and will grow increasingly valuable as more data become available.

Precise measurements of the stronger helium lines were therefore undertaken in order that they may serve as standards for the determination of other wave-lengths, and to furnish a basis for computations of theoretical interest.

II. *Measurement of Wave-lengths.*

1. *Direct Determinations from the Red Cadmium Line.*—Wave-lengths of 21 of the stronger helium lines were measured with the Fabry and Perot type of interferometer, which consisted of two partially reflecting plane surfaces held a few millimetres apart, and exactly parallel by an invar separator, using the practice previously adopted by the Bureau (*Bulletin*, 1915, xii., 179; 1916, xiii., 245). The interference rings formed by the action of the parallel planes of the interferometer upon the incident light were projected upon the wide slit of a spectrograph having a single prism of rock salt, portions of them accordingly being observed as short bars across the spectral lines. The specially designed achromatic lenses allowed a great range of wave-lengths to be photographed with one exposure. Thus, 2945 A and 5875 A (D_3) were obtained on one plate, as were also 3888 A and 7281 A.

The helium tube employed is similar in every way to the neon tube described by Meggers (*Bulletin*, 1913, xii., 202). It was filled at the Bureau with helium obtained from a London firm. The electrical excitation was furnished by stepping up from commercial alternating current of 110 volts, 60 cycles, to about 10,000 volts (on open circuit). Primary currents from 0·5 to 1·75 a were used, causing from 3 to 11 ma through the tube. The dark space was from 1 to 2 mm. in width.

Several of the helium wave-lengths were compared directly with the fundamental standard by photographing the cadmium and helium spectra simultaneously upon the same plate. The cadmium lamp, electrically heated to about 300° C., was in the optical axis of the spectrograph, while the beam of helium light was brought into the axis by reflection from a partially transparent surface through which the cadmium light passed. This surface was formed by a thin film of nickel which had been cathodically deposited upon a quartz disk. Two series of photographs were made in this way, in one case the interferometer films being of copper deposited on glass and in the other of nickel on quartz. The copper interferometers employed were of 5, 10, and 20 mm. separation, the nickel of 5, 10, 15, and 20 mm. The plates (Seed 27) were sensitised to the less refrangible rays by treating them with a solution containing dicyanin, pinaverdol, and ammonia. Exposures were made ranging from four to fifteen minutes and with varying amounts of current through the tube. The results are tabulated in Table I. The agreement of the two series is considered satisfactory except in the case of 7065 A. No other reason, however, than accidental error of observation can be assigned for this difference.

The very small corrections to reduce the wave-lengths to standard conditions (760 mm., 15° C.) were applied.

2. *Relative Measurements.*—The values in Table I. served for the determination of other helium lines on photographs of the helium spectrum alone. In this series the nickel films and separations of 3, 5, 7·5, and 15 mm. were used with exposures from twenty seconds to one hour.

With the exception of the three red lines which were not observed in this series, the ratios of wave-lengths in Table I. were satisfactorily confirmed, and are apparently accurate to 1 part in 4,000,000. The combined results of all the measurements made in this investigation appear in the first column of Table II.

TABLE I.—*Helium Wave-lengths by Direct Comparison with* Cd 6438 4696.

Copper films.	Nickel films.	Adopted.
3888·646	0 646	0·646
—	(4026·190)	—
4471·476	0·478	0·477
4713·143	0·143	0·143
4921·928	0 929	0·929
5015·675	0 675	0 675
(5047 734)	—	—
5875 616	0·618	0·617
6678 148	0·149	0·149
7065·186	0·190	0·188
7281·350	0·348	0·349

TABLE II.—*Collected Helium Wave-lengths.*

Bureau of Standards.	Rayleigh (a)	Rayleigh (b)	Eversheim.	Runge and Paschen.
2945·104	—	—	—	106
3187·743	—	—	—	701
3613 641	—	—	—	641
3705·003	—	—	—	007
3819 606	—	—	—	605
3888·646	—	—	—	638
3964 727	—	—	—	727
4026·189	—	—	—	192
4120·812	—	—	—	821
4143·759	—	—	—	766
4387·928	—	—	—	934
4437·549	—	—	—	549
4471·477	(478)	480	493	475
4713·143	(171)	142	154	074
4921 929	925	928	922	919
5015·675	680	678	683	556
5047 736	—	—	—	641
5875·618	616	623	639	650
6678·149	144	147	151	14
7065·188	189	197	207	22
7281·349	—	—	—	53

From the number and internal agreement of the individual determinations it seems that an error larger than 0·003 A is scarcely to be expected, and that probably most of the errors are smaller than that amount. In the case of the double lines the value, of course, refers to the stronger component. The weaker component seems to have been practically without effect upon the measurements, since accordant values were obtained from a considerable range both of effective exposures and of orders of interference.

This may be illustrated by the values obtained for D_3. It was customary to put several exposures of varying length upon each plate. Determinations of the difference between overexposed and normal or weak images are hence available for several plates. In units of a thousandth of an angstrom they run 0, 0, +1, +1, −3. +4, −5, the last three depending on a poor measurement in each case. The systematic difference is not larger than the accidental error. The photographs of helium alone were taken upon Seed 27 emulsion (not stained), but the longest exposure on each plate (about an hour) shows D_3 faintly. The wave-lengths of this line from four of these under-exposed images are practically in agreement with the other determinations, there being possibly a tendency toward a slightly higher value. For 5015 A, a single line, the difference, strong minus weak exposure, is 0·000 or ±0·001 A in 11 cases out of 13. The agreement of different interferometers is shown for two lines by

TABLE IV.—*Series Constants.*

$$n\ (\text{vac.}) = A - \frac{B}{m^2} - \frac{C}{m^4}.$$

Constants Computed from m = 3, 4, 5, in each Series.

	First group.			Second group.		
	Principal.	First subordinate.	Second subordinate.	Principal.	First subordinate.	Second subordinate.
A	38 469·22	29 225·53	29 147·13	32 030·82	27 176·66	27 154·51
B	110 501·7	109 845·2	102 963·4	109 518·3	109 783·2	107 878·3
C	13 027·4	152·7	96 030·4	−1 887·8	226·2	38 826·8

Observed Minus Computed (Angstroms).

M	—	—	—	—	—	—
2	−18·2	—	—	+124·3	—	—
3	0	0	0	0	0	0
4	0	0	0	0	0	0
5	0	0	0	0	0	0
6	+0·18	+0·021	−1·06	−0·030	+0·013	−0·34
7	+0·34	+0·047	−2·2	−0·091	+0·036	−0·71
8	+0·45	+0·078	−3·2	−0·103	+0·022	−1·07
9	+0·56	+0·096	−4·0	−0·19	+0·068	−1·30
10	—	+0·134	—	−0·21	+0·069	−1·54
11	—	—	—	−0·23	+0·072	—
12	—	—	—	—	+0·090	—

Table III., which refers entirely to the direct comparisons with cadmium. The small figures in parentheses give the number of exposures upon which the value depends.

TABLE III.—*Wave-lengths from Different Interferometers.* (Comparisons with cadmium).

	5015 A.		5875 A.	
	Copper.	Nickel.	Copper.	Nickel.
5 mm. ..	0·674 (2)	0·677 (2)	0·617 (3)	0·619 (3)
10 mm. ..	0·673 (3)	0·674 (2)	0·616 (3)	0·617 (2)
15 mm. ..	—	0·675 (5)	—	0·618 (6)
20 mm. ..	0·677 (3)	0·676 (3)	—	0·618 (3)

3.—*Elimination of Difference of Phase Change.*—The dispersion of phase change at reflection from the interferometer mirrors has been referred to as "one of the less agreeable features" of interference measurements. It is customary to find the amount of the differential effect for different wave-lengths by observations with large and small path differences, and to compute the small corrections to be applied to the measured wave-lengths. This procedure is, however, by no means necessary, as the whole effect can be eliminated by using differences, as was done by Priest for visual methods (*Bulletin*, vi., 573—Reprint No. 142, 1911). Let us find by the use of the standard line, say Cd 6438 A, the double thickness of a large and of a small interferometer. If the difference of these numbers be divided by the difference of the measured orders of interference for another line, it is obvious that the quotient will be the correct wave-length freed from any effect of difference of phase change without having found that quantity at all. The difference of the orders will be of about the same accuracy as the larger one, for while the percentage error of the smaller may be greater the actual numerical uncertainty is less.

The same final values should, of course, be arrived at whether the difference of phase change is eliminated as suggested above or determined by the usual methods and the proper corrections applied. This is the case in the present series of measurements.

III. *Comparison with Previous Values.*

The present measurements and those by Lord Rayleigh (*Phil. Mag.*, 1908 [6], xv., 548) are in quite good agreement as shown by Table II. Columns 2 (a) and 2 (b) are separate series, of which the second is to be given greater weight. Eversheim's values (*Zs. Wiss. Photo.*, 1909, viii., 148) are greater, but the differance are not uniform. Except for 3187 A the grating values of the shorter wave-lengths by Runge and Paschen (*Astroph. Jour.*, 1896, iii., 4) are in good accord with the interference results. The discrepancies among the longer wave-lengths are possibly due in some way to the fact that their measurements depend upon comparison lines in another order (second). This is the case for 4713, 4921, 5015, 5047, 5875, 5678, and 7065 A. The mean arithmetic residual Runge and Paschen minus Bureau of Standards for these lines is 0·052 A, as compared with 0·0065 A for the remaining lines, for which the comparisons were in the first order. Omitting 3187 A the mean residual for 12 of the shorter lines is only 0·003 A.

Using an interference method which depends upon observing the disappearance of the central ring (*Bulletin*, 1911, vi., 573—Reprint No. 142) Priest found the apparent wave-lengths of certain helium lines to vary with the amount of current through the tube. Variations of this kind were not observed by him for 5015 A (*Bulletin*, 1911, viii., 1—Reprint No. 179). Mr. Priest has kindly given me the exact value obtained by him for this line as 5015·679 A. This is the mean of several accordant measurements.

IV. *Series Relations.*

When our understanding of spectral series is complete the magnitudes of certain physical quantities can probably be computed from a single series, and from relations between different series, and it may be in this connection that accurate measurements of wave-length will finally be of the most value. In the meantime they can be used to determine the applicability of the various types of formula which have been suggested, to test the so-called "combination principle," &c. For obvious reasons the present investigation includes only a small number of lines at or near the beginning of each series. These lines, although favourably situated for the purpose, will not by themselves give the best values of the series constants, particularly of the convergence frequency. Hence no extensive recomputations have been undertaken at this time, but it was thought of interest to see how closely a three-constant formula based upon three consecutive well-determined lines would represent the remainder of the series.

None of the series can be represented exactly by a formula of the type

$$n = A - B/m^2,$$

where n is the reciprocal of the wave-length, m represents successive integers, A and B are constants. This equation however, gives a fairly close representation of the two first subordinate series (5875 A, 4471 A, &c.; 6678 A, 4921 A, &c.). The constant B is about the same for both and approximately 0·2 per cent larger than in the Balmer series of hydrogen.

It is well known that the Kayser and Runge formula,

$$n = A - B/m^2 - C/m^3,$$

will give a fair representation of the helium series. The lines for which $m = 3, 4, 5$, in each of the six series have been measured in the present investigation. The constants A, B, C, as computed from these three lines, appear in Table IV., which also contains the residuals of all the well-observed lines in each series.

In every instance the error of the representation even for $m = 6$ is very much larger than the uncertainty of observation, while the residuals show a fairly smooth and converging increase toward the terms of higher order. In some cases there is no improvement as compared with the series computed by Kayser and Runge from less accurate values. This is in agreement with the prevailing opinion that the formula contains the first three terms of a rapidly converging mathematical series which may be regarded as the expansion of a closed expression as yet unknown.

V. *Summary.*

Wave-lengths of 21 of the stronger helium lines have been accurately measured by interference methods. Nine of them were compared directly with the standard cadmium line.

The possibility of eliminating the effect of apparent variation of interferometer thickness with wave-length is noted.

The Kayser and Runge formula for spectral series, based upon three oonsecutive lines, will not reproduce accurately even the next member in any one of the six helium series

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NICKEL.

Canada's Share in the World's Supply.
The Future of Nickel Refining in Canada.

By E. B. BIGGAR.

The present dominant position of Canada in the world's nickel market was not realised when costly experiments were being made by chemists connected with the big nickel corporations to overcome the difficulties of smelting the ores of the Sudbury district. The chief source of the world's supply then was Europe, and even the United States surpassed Canada. From 1840 to 1860 the production of the whole world only averaged from 100 to 200 tons a year, and its use was chiefly for cheap jewellery and utensils that could be produced from the alloy known as German silver. Its price averaged 2 dols. to 3 dols. a pound; but this increased by the growing demand and the uncertain supply, till in the seventies when it averaged 6 dols. to 7 dols. a pound. This rise was largely caused by the adoption by Germany, the United States, and some other countries, of a nickel alloy for coinage, which used up more nickel than could be replaced by the annual supply.

As the technical problems of working the metal and making alloys were solved, and its new qualities became known, the demand and the supply both increased, but improved processes enabled the smelters and refiners to cheapen the product and still make more profits than before. The nickel refining corporations have been making prices ranging from 30 to 45 cents per pound, according to the size of the order.

As mining and exploration have proceeded in Canada the extent and richness of the Canadian nickel ores appear to be more clearly demonstrated, while the supplies from other sources have become more fitful by reason of the pockety nature of the deposits and their limited area.

No one knows what nickel deposits remain to be discovered; but the present situation is that there are no known mines that seriously compete with Canada extent. It was in 1889 that nickel first appeared as separate article of Canada's exports with over a third the estimated production of the world.

For example, the most promising nickel mine of the United States, the Gap Mine of Pennsylvania, has been practically out of production for twenty years, and of the several States having deposits not one has been producing nickel ore for the past three years. The only nickel produced in the United States is that recovered as a by-product of "blister" copper ores, amounting to about 250 tons of metal a year. The Swedish mines were closed when the war broke out, though they are now operating on a small scale, no doubt helping to make up the shortage in Germany. The output of Norway averaged less than 70 tons a year of refined metal before the war, and the Norwegian ores only averaged 2 per cent of metal. The Norwegians are successful smelters, but they use imported ore largely, much of it from New Caledonia. The deposits of Norway, which were out of business when war was declared, have produced from 240 to 690 tons annually since the war. There are deposits in the Ural mountains in Russia which are said to be producing 600 tons a year, and there are deposits in Australia and South Africa producing a few tons each in 1916.

The output and export trom New Caledonia are very jumpy quantities, varying from 70,000 to 125,000 tons of ore and matte per year, producing 2000 to 4000 tons of pure metal. Out of 800 nickel mining concessions granted in New Caledonia only 40 are actually exploited, and the exports of ore during the last half dozen years have decreased; but whether this is altogether due to mining conditions or to the policy of the International Nickel Company of the United States, which has acquired large interests in these mines, and to whom much of that ore goes for refining in New Jersey, is not clear. One reason why the New Caledonia mines may not be able to maintain production in competition with Canada is that all the materials for smelting and refining—such as coal, soda ash, gypsum, and sulphur—have to be imported, while the long sea voyages both for materials and the shipments of ore or metal are a drawback. At all events, M. du Paizat, a French authority, estimated the output of the threee smelters of New Caledonia to be equivalent to 2263 tons in 1912, and the annual average production has remained at about that since 1891. Compare this with an output equivalent to 42,500 tons of pure nickel by Canada in 1916.

The following table shows the eminence Canada has achieved as a nickel-producing country.

Nickel Production in Canada and the World.

	Production of Canada. Tons.	Production all other countries. Tons.		World's production. Tons.
1840-60 ..	—	—	An average of	200
1860-70 ..	—	—	" "	600 to 700
1889	415	1,085		1,500
1890	713	1,287		2,000
1894	2,453	2,547		5,000
1902	5,346	3,254		8,600
1906	10,776	3,524		14,300
1910	18,636	2,364		21,000
1914	22,759	7,241*		30,000
1915	34,039	4,000		38.039
1916	42,000	4,000		46,000

* Est.

The significance of these figures consists not so much in the fact of the extraordinary increase in the output of the Canadian mines, as in the fact that all the increase in the world's supply in recent years has been contributed by Canada alone. The rest of the world has indeed decreased its output during the past three years.

With the exception of a small quantity refined at Thorold, all the nickel mined in Ontario is shipped abroad as “matte” containing the copper with the nickel, and the next stage in the industry will be the establishment of refineries in Canada which will carry the processes of manufacturing in all their ramifications to the finished articles. The most interesting development in this branch is the acquisition of the properties of the Canadian Nickel Corporation, including the Murray mine, by the British American Nickel Company, which will establish both smelters and refineries in Ontario. The new company has a ten-year contract from the Imperial Government for a large quantity of nickel, but the important feature of their operations will be the use in Canada of the refining process worked out by V. Hybinette, and in successful use at Kristiansand, Norway, for the last six years. By this nickel is refined to a purity of 98·70 per cent, and at a cost of about 13 cents a pound, the metal selling at 40 cents to 45 cents per pound. It is expected that these works, which are located on the celebrated Murray mine, four miles from Sudbury, will be in operation within a year, and the effect will be to establish the nickel industry for the first time on a Canadian foundation.

The International Nickel Company of the United States are also erecting refineries in Canada at Port Colborne, Ont., where new works planned to cover 350 acres are now in progress.

The largest share of the nickel mined in Canada—and consequently the largest share of the world's supply—has hitherto been smelted by the Canadian Copper Company, which is owned by the International Nickel Company. The Canadian Copper Company at its works in Sudbury, smelts the ore into a matte (a French word meaning dull, or without gloss), comprising chiefly the copper, nickel, and silver contents, but separated from its coarser metals. The matte is then shipped to the International Nickel Company's works at Constable Hook, N.J., where it is refined, and this refining work employs a large number of skilled hands, and involves the chief industrial processes connected with the nickel trade. This corporation controls not only the Canadian material and the extraction of nickel from United States copper, but it owns the Nickel Corporation, Ltd., and the Société Minière Caledonienne, both of New Caledonia, which two companies now own 9217 hectares of mineral land and 3848 hectares of other land in that island, and hence the peculiar fact of so large a part of the New Caledonia ores being shipped all the way around the world to New Jersey for refinement. The matte product from the Canadian Copper Company and the product of refined nickel from the New Jersey works of the parent company make about two-thirds of all the nickel output of the world.

The capital of the International Nickel Company is 62,000,000 dols., and its net profits range between four and five million dollars a year—the figures for 1915 were 5,598,071, and for 1916—over seven millions—besides reserve sums and funds laid by for furthur exploitations. Its wholesale customers are the chief governments of the world, and needless to say that fact gave it control of the world's market prices and the world's supply.

The International Nickel Company has control, but it has not an absolute monopoly of the world's nickel industry. The Mond Nickel Company, operating by another process worked out by Dr. Ludwig Mond, a British member of Parliament, owns considerable nickel areas in the Sudbury district, has a smelter at Coulson in that district, and ships its matte to Clydach, near Swansea, Wales, for refining. Its chief customers are the British and allied Governments. Its capital is £2,410,000, and on some classes of stock it has paid dividends ranging from 48 to 55 per cent. Then there is the Alexo Mine, on the Porcupine branch of the T. and N.O.R., Temiskaming district, which ships some ore to the Mond smelter, and there are a dozen other companies which own nickel lands but are not yet smelters or refiners.—*Canadian Chemical Journal.*, i., No. 3.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

By IRVING LANGMUIR.

(Continued from p. 104).

So far we have considered the evaporation of solids which give monatomic vapours. When a crystal such as sodium chloride evaporates the atoms must group themselves together in pairs *before* they escape from the surface forces.

The latent heat of evaporation does not correspond to the energy required to separate the atoms from each other, but only to the energy needed to separate one group of atoms from other similar groups. This makes it appear that evaporation in these cases is the result of a tautomeric change taking place among the surface atoms. Thus in the case of solid sodium chloride the sodium atoms are ordinarily held to the adjacent chlorine atoms by secondary valence. If, however, a tautomeric change occurs by which a pair of adjacent chlorine and sodium atoms become attached to each other by *primary* valencies, then this pair will be held to the surface by much weaker forces than those holding other atoms not so combined. The pairs held by primary valencies may thus be enabled to evaporate from the surface. We should not assume, however, that every pair of atoms so combined, or even the majority of them, will evaporate, for if we do it would follow that only a very small fraction of molecules of salt vapour striking a surface would condense. It is more likely that the tautomeric changes take place with high frequency, but that the time during which a pair of atoms exists consecutively in the tautomeric form is comparable with the time of relaxation; that is, of the order of 10^{-17} seconds. Now, the time required for an atom or a group of atoms to move out of the region of attractive forces (a distance of about 10^{-8} cm.) must be *at least* 10^{-14} seconds, since molecular velocities are always less than 10^{6} cm. per second. We are thus led to believe that a sodium chloride molecule only evaporates when the tautomeric change occurs at a moment when the atoms are already displaced from their equilibrium positions to an unusual degree.

The evaporation of compound substances of the polar type thus involves rather complicated chemical changes in which the atoms rearrange themselves according to their primary valencies. This conception of the mechanism of evaporation receives support from the fact that so few complex polar compounds or molecular compounds can be volatilised without dissociation. Thus, nearly all inorganic salts except those which are compounds of the first order (halide salts, for instance) are decomposed or dissociate on heating. Crystals containing water of crystallisation can never be distilled with their water of crystallisation. Even compounds like sulphuric acid give vapours which are dissociated.

Non-polar compounds, such as most organic substances, usually contain fixed molecules which, even in the solid condition, are held together by primary valencies, the secondary valencies merely serving to hold the fixed molecules together. In this case evaporation involves only a breaking of the secondary valence forces so that it becomes quite similar to the evaporation of metals or other substances giving monatomic vapours.

Relation between Condensation and Evaporation.—When a solid is in equilibrium with its own vapour, condensation and evaporation are occurring simultaneously at equal rates. We have seen that we are justified, in the majority of cases, in considering that all the molecules of vapour which strike against the surface condense (are not reflected).

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* From the *Journal of the American Chemical Society*, xxxviii No. 11.

Now the rate at which the molecules strike the surface is given by Equation 4,—

$$m = \sqrt{\frac{M}{2\pi RT}}\,p \quad . \quad . \quad . \quad . \quad , \quad . \quad (4).$$

Since all of the molecules condense, and since the rate of evaporation must be equal to the rate of condensation, we may use this same equation to calculate the rate of evaporation, m, in terms of the pressure p, of the saturated vapour. If the condensation and evaporation go on independently of one another then Equation 4 should give a means of calculating the rate at which a solid evaporates into a perfect vacuum. Or, conversely, if we determine the rate of evaporation of a solid in a high vacuum we can calculate the vapour pressure by the above equation. (The writer, together with Mr. G. M. J. Mackay, has used this method for measuring the vapour pressures of the metals tungsten, platinum, molybdenum, iron, nickel, copper, and silver, and the results have been, or will be, published in the *Physical Review*. The reasons which justify the assumption that the reflectivity is negligible are given in detail in a recent article—*Physical Review*, 1916, viii., 149).

This theoretical relation between the rate of evaporation and vapour pressure was first obtained by Hertz (*Ann. Physik.*, 1882, xvii., 177). Hertz himself and others who have used the equation have not considered that the reflectivity is negligible and hence looked upon the calculated value of m as being greater than the true rate of evaporation.

R. Marcellin (*Ann. Phys.*, 1915, iii., 185) has recently attempted to measure the maximum rate of evaporation of naphthalene, nitrobenzene, and iodine in a vacuum, and compared his results with those calculated by Equation 4. He concludes that at 40° only about one molecule out of twenty striking the surface condenses, while at 70° about one out of five condenses. That is, the reflectivity decreases rapidly at higher temperatures. It should be noted, on the other hand, that R. W. Wood finds no reflection of mercury atoms from a surface at very low temperatures, but concludes that the atoms are all reflected at higher temperatures (*Phil. Mag.*, 1915, xxx., 300).

Marcellin measured the rates of evaporation of substances in capillary tubes. By plotting the rate of evaporation against the length of the tube through which the vapour had to pass, he *extrapolated* back to zero length of tube, and expected in this way to find the rate of evaporation in a perfect vacuum. When we consider that this extrapolation was carried out over a length of tube at least eight times the diameter of the tube, we realise how very few of the molecules evaporating from the surface could have escaped from the end of the tube. The great majority of them must have struck the walls of the tube, and thus have been afforded an opportunity of returning back on to the surface. Measurements of this sort, to have any value, must be made so that molecules evaporating from the surface may move off in straight lines without meeting any obstruction until they strike the cooled surface on which they permanently condense.

If Marcellin had plotted the reciprocal of the speed of evaporation (which should be a linear function of the length of the tube) instead of the speed itself, it would have been apparent, first, that the observed rates were much lower than the true maximum rates, and, second, that even with the small capillaries he used he did not succeed in keeping the temperature of the evaporating surface up to that of the bath surrounding the tube. Therefore, it appears that Marcellin's experiments are entirely consistent with the view that the true rate of evaporation is accurately given by Equation 4.

The writer has also shown (*Phys. Rev.*, *loc. cit.*) that Wood's experiments may equally well be explained by assuming, instead of a reflection of mercury atoms at the higher temperatures, a condensation followed by evaporation.

For the case of a clean surface of liquid mercury evaporating into a good vacuum Knudsen has recently proved that Equation 4 gives the actual rate of evaporation (*Ann. Phys.*, 1915, xlvii., 697).

Wood makes the statement that atoms of mercury which are "diffusely reflected" (or, according to our theory, condensed and re-evaporated) from a surface do not seem to be distributed quite according to Lambert's cosine law, but there seem to be [illegible] few atoms leaving the surface in directions nearly parallel to the surface. Now, if evaporation and condensation can go on simultaneously, although independently, it must follow, according to Maxwell, that the number of atoms leaving the surface in different directions must be proportional to the projected area in that direction (Lambert's cosine law).

Observations on the evaporation of metals in high vacuum have convinced the writer that Lambert's cosine law does hold accurately for evaporation, and the Wood's conclusion is incorrect.

Wood drew his conclusion from the *apparent* sudden decrease in the thickness of a film of metal deposited on glass in the region close to the plane of the surface from which "reflection" took place. In the writer's experience this sudden decrease which he has often observed, and which certainly seems very real, is only apparent. It is due to the fact that although the *thickness* of the film varies *linearly* with the distance from the plane of the surface the *light absorption* varies *exponentially*.

Kaye and Ewen (*Proc. Roy. Soc.*, A, 1914, lxxx., 58) have reported that at pressures of a few mm. of gas the sublimation from heated metals (Fe, W, Cu, Ag, or Ir) appear to consist of two parts, one of which diffuses like a gas, but the other, often the larger part, is projected in straight lines in a direction perpendicular to the surface at which it originates. In the experience of the writer such effects are due to convection currents (which often produce very freakish effects at pressures of a few mm.), or to electric discharges through the gas. They are usually enormously stimulated by the presence of traces of moisture. In a thoroughly dry gas or in a good vacuum, and in the absence of electric discharges, the evaporation of heated metals takes place without any evidences of such "projection" of particles in definite directions. Of course, in a really good vacuum the atoms leaving the heated surface travel in perfectly straight lines until they strike an obstacle, and in this way "shadows" of interposed objects may be obtained. But this projection of particles takes place according to Lambert's cosine law and is in full accord with the ordinary conception of the kinetic theory.

We have assumed so far that evaporation and condensation can go on simultaneously without influencing each other. For example, in calculating by Equation 4 the rate of evaporation in a vacuum from the pressure of the saturated vapour we had to assume that the true rate of evaporation in presence of saturated vapour is the same as that in vacuum; in other words, that the condensation of the vapour has no effect on the rate of evaporation.

There are, however, reasons which might lead us to expect a difference in the rate of evaporation in presence of and in the absence of vapour.

In the first place when a vapour atom or molecule condenses on a surface an amount of energy corresponding to the latent heat of evaporation must be liberated, and must result in a local rise of temperature. It would seem that this might cause the evaporation of an adjacent atom which would otherwise not evaporate. Thus the condensation of vapour might stimulate the evaporation. This would be equivalent in many ways to a reflection of vapour molecules from the surface.

The following considerations make it very improbable that condensation has any such effect on evaporation. The "average life" of an atom on a surface may be readily calculated from Equations 4 and 6. The life will be inversely proportional to the vapour pressure, and will be proportional to $\sqrt{MT}$. If we choose $M = 25$, $T = 400$, and p = one megabar (atmospheric pressure) and assume that $N_0 = 10^{15}$ atoms per sq. cm. we thus calculate that the life of an atom on the surface would be $3\cdot8 \times 10^{-9}$ seconds. In the evaporation of substances in vacuum the equilibrium pressure would always be extremely small compared to one megabar, so that the life of the atoms on the surface would be much more than 10^{-8} seconds. Now, the time taken by an atom to receive or give up its energy to adjacent atoms is of the order of 10^{-17} seconds, or about 10^{+9} times less than the life of the atom on the surface. These figures show that the critical conditions necessary to cause the evaporation of an atom are of relatively rare occurrence. The chance is negligibly small, therefore, that an atom condensing on the surface will be able to give up its energy to an adjacent atom at a moment when the latter is nearly in its critical condition.

These considerations make it appear probable that the energy liberated by the condensation of vapour is totally without influence on the mechanism of evaporation.

There is, however, another kind of effect by which condensation may, and probably does, influence the rate of evaporation. Let us consider, for example, solid naphthalene in contact with its saturated vapour. When a molecule of naphthalene vapour strikes against the surface of the crystalline substance it undoubtedly condenses in the position in which it strikes. The chances are small that this position will be one in which the molecule forms a continuation of the space lattice of the crystal. If the temperature is sufficiently high the molecule may, by a sort of sintering process, readjust its position in conformity with the underlying group of molecules. But at lower temperatures this readjustment will often be impossible.

Such irregularly placed molecules will tend to evaporate from the surface more rapidly than those in the regular lattice positions.

We have already seen that this greater rate of evaporation manifests itself in the tendency for larger and more perfect crystals to be formed, as the sublimation of a substance is made more nearly reversible.

Since the rate of evaporation of the irregularly placed molecules must be finite it follows that the surface must be more or less completely covered by such molecules. In other words, the surface of a crystalline solid in equilibrium with its saturated vapour may be covered by a layer of irregularly placed molecules; in other words, there may be an amorphous surface film.

The extent to which the surface is covered by such a film will depend upon the ease with which the molecules rearrange themselves, and also upon the relative rates of evaporation of the regularly and irregularly placed molecules.

It is of interest to consider the evaporation and condensation of a crystal of naphthalene under various conditions:—

1. *Irreversible Condensation.*—If a stream of naphthalene vapour is admitted at low pressure into a well exhausted bulb immersed in liquid air, we should expect that all the molecules would condense in the positions in which they first strike the cooled bulb. The condensed material should then be wholly amorphous, both on its surface and in its interior.

2. *Irreversible Evaporation.*—If a naphthalene crystal is suspended in an exhausted bulb and the latter is immersed into liquid air, the naphthalene crystal will evaporate irreversibly, since no molecules of naphthalene will return from the surface of the bulb. In this case there will be no amorphous surface layer on the crystal.

3. *Reversible Evaporation or Condensation.*—If a naphthalene crystal is placed on one arm of an inverted and exhausted U-tube and the other arm is maintained at a very slightly lower temperatare, the naphthalene will slowly sublime from one arm to the other and form crystals in the cooler arm. These crystals as well as the one in the warmer arm will have amorphous surface layers.

If we calculate the rate of evaporation from the pressure of the saturated vapour by Equation 4, we obtain a value which corresponds to the rate of evaporation from the amorphous surface layer, and not from the true crystalline surface. Therefore the rate of evaporation of a crystal in a good vacuum (Case 2, Irreversible Evaporation) should be lower than that calculated from the vapour pressure, notwithstanding the fact that no reflection of molecules from the surface takes place.

It is probable that in the great majority of cases, especially with substances such as metals which give monatomic vapours, that this effect is entirely negligible, because of the great ease with which the atoms can arrange themselves on the surface.

(Note.—According to the principle already enunciated, by which every element in the mechanism of a reversible process must itself be reversible, it follows that any rearrangement of molecules on the surface, which takes place during the condensation of a vapour, most take place to the same extent, but in the reverse direction, in the evaporation of the substance. Thus, if molecules rearrange themselves into regular positions an equal number of molecules must be continually leaving regular positions to assume irregular positions. This leads to the conclusion that even with substances which give monatomic vapours the surface must in part be amorphous. However, an amorphous structure due to this cause will be present to the same extent when the evaporation is irreversible as it is in the case of reversible evaporation. Therefore no error is made in calculating the rate of evaporation in a vacuum from the vapour pressure, according to Equation 4).

Even with substances having molecules as complicated as that of naphthalene it seems improbable that the difference between the rates of evaporation of crystalline and amorphous surfaces would be great enough to very seriously affect the validity of Equation 4 when applied to the calculation of the rate of evaporation in a vacuum. Accurate experimental determinations of the rates of evaporation of complex organic compounds in high vacuum should prove of great interest.

There are cases, however, where we may expect very radical differences between the true rates of evaporation *in vacuo* and the rate calculated from the vapour pressure by Equation 4.

Red phosphorus should furnish an example of this sort. The transformation of yellow into red phosphorus takes place very much more slowly than the rate at which molecules of phosphorus vapour strike against a surface of red phosphorus. Therefore the molecules of phosphorus vapour which impinge against the surface and condense must evaporate again without having been in the condition of red phosphorus.

The surface of the red phosphorus is therefore covered, at least in part, by a layer of fixed molecules which constitute an adsorbed film of yellow phosphorus. The rate of evaporation calculated by Equation 4 corresponds to the evaporation from this adsorbed film of yellow phosphorus plus that from the uncovered portion of the surface of red phosphorus. On the other hand, if the red phosphorus is placed in a good vacuum the adsorbed film of yellow phosphorus will distil off, and the observed rate of evaporation will correspond to the rate of conversion of red into yellow phosphorus. This rate will be very much less than that calculated from the equilibrium pressure.

It is thus probable in the case of red phosphorus that the equilibrium pressure is not a true vapour pressure in the ordinary sense, but is rather to be regarded as a dissociation pressure.

The rate of evaporation of ammonium chloride in a vacuum, both in the presence of and in the absence of traces of moisture, should throw a very interesting light upon the mechanism of the evaporation or dissociation of this substance (see papers by Abegg and Johnson, *Zeit. Phys. Chem.*, 1908, lxi., 455; Scheffer, *Proc. Akad. Wetenschappen Amsterdam*, 1915, xviii., 446).

(To be continued).

COAL-TAR.[*]

The Minister of Munitions in exercise of the powers conferred upon him by the Defence of the Realm Acts and of all other powers enabling him hereby Orders as follows:—

1. No person shall as and from October 1, 1917, until further notice purchase or offer to purchase any coal tar (whether crude or dehydrated) except under and in accordance with the terms and conditions of a licence issued by or under the authority of the Minister of Munitions. Provided that no License shall be required—

(*a*) By a tar distiller for the purchase of coal-tar in any quantities, provided that the whole quantity purchased is intended to be and is in fact distilled by such distiller.

(*b*) By any person for the purchase of coal-tar (whether crude or dehydrated) in quantities not exceeding ten gallons provided that the total quantity purchased by any one person during any one calendar month does not exceed 50 gallons.

2. No person shall as from October 1, 1917, until further notice except under and in accordance with the terms and conditions of a licence issued by or under the authority of the Minister of Munitions accept delivery of or make payment for any coal-tar tendered for delivery under any contract existing at the date of this Order unless (a) such contract is in writing and (b) full written particulars of such contract have been furnished to the Minister of Munitions before October 1, 1917, by the person for the time being entitled to deliveries thereunder.

3. For the purpose of this Order the expression "coal tar" shall mean and include tar produced or derived from the destructive distillation of bituminous material by any means other than blast furnaces.

Note.—All applications in reference to this Order (including applications for licences) should be addressed to the Ministry of Munitions, Department of Explosives Supply, Storey's Gate, Westminster, S.W. 1, and marked "E.G.S."

CREDIT FOR FARMERS.[†]

Arrangements have now been concluded with the banks, under which credit will be given, on the recommendation of County Agricultural Executive Committees, for the purchase of any requirements necessary for the increase of food production, including seeds, artificial manures, working horses, machinery, and implements, but not for the payment of wages.

Application should be made to the Secretary of the Agricultural Executive Committee for the Administrative County within which the applicant's land is situated, on a form to be obtained from the Committee.

On the approval of an application by the Committee, the applicant will be authorised to order what he requires, and to send the bill to the Bank nominated to make the advance. The Bank will settle the account, and treat the amount as a special overdraft, repayable under Government guarantee, taking from the applicant a promissory note in the usual form.

Overdrafts will be charged with interest at the rate of 5 per cent per annum, and will, as a rule, be granted for a period of nine months, but at the expiration of that period may be renewed for a further period.

Co-operative Societies equally with individual applicants are eligible for the grant of credit under this scheme.

The addresses of the Agricultural Executive Committees for the various Counties of England and Wales, and the names of the Banks participating in the arrangement, are shown in the leaflet.

PRIESTLEY MEMORIAL COMMITTEE OF THE AMERICAN CHEMICAL SOCIETY.

By resolution of the Council of the American Chemical Society adopted at its meeting in Urbana in April, 1916, the President was requested to appoint a Committee to devise and carry out a plan for a suitable memorial to Joseph Priestley. After careful consideration of various plans, the members of the Committee desire to present the following recommendations to the Society:—

1. That a bust portrait of Joseph Priestley be secured, to be a copy of the best available portrait; that this be retained as the property of the American Chemical Society, but be deposited as a loan in the National Museum in Washington. Also,

2. That a gold medal be awarded at intervals of probably more than one year for superior achievements in chemical research; the award to carry with it the requirement that the recipient shall deliver an address before the General Meeting of the Society at the time of the presentation or at such other time and place as the Council of the Society may direct.

Careful inquiry has convinced the Committee that, in order to carry out these plans a fund of at least 2000 dols. should be secured. It is requested that subscriptions be sent to the Chairman or to any member of the Committee. Contributions of sums from 1.00 dols. upwards are asked.

Joseph Priestley was born at Fieldhead in England in 1733. Although educated for the ministry he became noted as a teacher and lecturer on natural science, and especially as an investigator in chemistry, devoting his attention largely to the study of gases. Persecuted and shunned as a result of popular prejudice for his theological views as a dissenter from the Established Church, he migrated to America in 1794 and settled with his family in Northumberland, Pennsylvania. Here he established a laboratory and continued his work as an investigator in chemistry.

While famous throughout Europe and in America for his historical and philosophical writings, for his important work on the History of Electricity, and many other contributions to scientific literature, he is more especially known to modern chemists for his researches on the chemistry of gases, which culminated in 1774 in the discovery of oxygen, described in his treatise entitled "Experiments and Observations on Different Kinds of Airs."

He continued in America to be a contributor to scientific and theological literature until his death in Northumberland in 1804.

On July 31, 1874, many of the leading chemists of America met near the grave of Joseph Priestley at Northumberland to honour the memory of the man who had discovered oxygen one hundred years before. In the account of the proceedings detailed in the *American Chemist* for 1874, we are told that a movement was there begun which led later to the establishment of the American Chemical Society.

And as the foundation of the American Chemical Society has been thus linked with the name of Joseph Priestley, it would seem proper that we should seek in some lasting way to commemorate his work as an investigator and philosopher and tireless searcher after truth.

It is earnestly hoped that the plans now proposed by the Committee for a memorial will meet with approval and that we shall be able, by means of an adequate subscription fund, to render such honour as is due to the memory of Joseph Priestley.

Committee—

F. C. Phillips, Chairman, University of Pittsburgh, Pa.

M. T. Bogert, National Research Council, Munsey Buildings, Washington, D.C.

E. D. Campbell, University of Michigan, Ann Arbor, Mich.

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[*] Ministry of Munitions of War, Whitehall Place, S.W. 1, September 4, 1917. Press Bureau Order

[†] Board of Agriculture and Fisheries, Food Production Leaflet No. 2. (Copies of this leaflet may be obtained, free of charge and post free on application to the Secretary, Board of Agriculture and Fisheries, 3, St. James's Square, London, S.W. 1. Letters of application so addressed need not be stamped).

C. F. Chandler, New Hartford, Conn.
F. W. Clark, U.S. Geological Survey, Washington, D.C.
E. C. Franklin, Leland Stanford, Jr., University, Cal.
J. L. Howe, Washington and Lee University, Lexington, Va.
H. Long, 2421 Dearborn Street, Chicago, Ill.
Edward W. Morley, West Hartford, Conn.
A. A. Noyes, Mass. Institute of Technology, Boston, Mass.
W. A. Noyes, University of Illinois, Urbana, Ill.
Ira Remsen, Johns Hopkins University, Baltimore, Md.
E. F. Smith, University of Pennsylvania, Philadelphia, Pa.
Alfred Springer, 312 East Second Street, Cincinnati, O.
F. P. Venable, Chapel Hill, N.C.

NOTICES OF BOOKS.

Soil Conditions and Plant Growth. By Edward J. Russell, D.Sc. (Lond.), F.R.S. Third Edition: London, New York, Bombay, Calcutta, and Madras. Longmans, Green, and Co. Pp. viii+243. Price 6s. 6d. net.

The study of the soil as a medium for plant life has hitherto been undertaken in a rather haphazard manner, and Dr. Russell's work, in attempting to systematise it, is particularly valuable both from the practical and theoretical points of view. By his own investigations he has added much material to the science, and in this book he has admirably summarised, criticised, and explained practically all the work that has been done here, in America, and on the Continent. The fact that the first edition was translated into German shows that its value was recognised abroad. In the third edition a new chapter discusses the colloidal properties of the soil. Presupposing a knowledge of the properties of colloids the author shows how far far they are exhibited by soils, and explains their effects as far as they have been studied. The question of the constitution of the soil is briefly discussed and the work of the American investigators of the subject is reviewed. Other parts of the text have been much expanded, and the excellent bibliography has been brought up to date.

Annals of the Royal Society Club. By Sir Archibald Geikie, O.M., K.C.B., D.C.L., Past-President of the Royal Society. London: Macmillan and Co., Ltd. 1917. Pp. xv+504.

The history of the Royal Society Club, which has been in existence for at least 174 years, will be read with interest by many of the general public; it throws light upon the habits and customs of the intellectual classes in England in the eighteenth and nineteenth centuries, besides giving an insight into the state of scientific thought in these times. The author has given an account of the history of the club year by year, and has provided many biographical details of the men of science and others who were members or guests of the club. Some forty portraits are included from the collection of engraved portraits belonging to the Society. The preparation of the history involved the careful scrutiny of the records of the club, and also the study of contemporary literature and of the "Dictionary of National Biography," and Sir Archibald Geikie has welded together the vast amount of material he collected to make a highly entertaining volume of permanent value. The book is one which can be read through with sustained interest from the first page to the last, while the possessor of it will undoubtedly constantly want to dip into it for information and enjoyment.

Chemistry in the Service of Man. By Alexander Findlay, M.A., D.Sc., F.I.C. Second Edition. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1917. Pp. xv+272. Price 6s. net.

It is highly satisfactory to find that a second edition of this book is required in only a little more than a year from the issue of the first. The classically educated but scientifically ignorant public are showing signs of awakening interest in natural science, and can evidently be reached by the right kind of book, such as this work has emphatically shown itself to be. There is little need to call the attention of the readers of the Chemical News to its excellence, for the second edition is practically a reproduction of the first, with the addition of a new chapter on fermentation and enzyme action, in which the *rôle* of enzymes in nature and in the industries is discussed, and an account is given of the manufacture of alcohol and alcoholic beverages.

Industrial and Manufacturing Chemistry. Part II. *Inorganic.* By Geoffrey Martin, Ph.D., D.Sc., F.I.C., F.C.S., assisted by various specialists. Vol. II. London: Crosby Lockwood and Son. 1917. Pp. xvi+482. Price 25s. net.

The second volume of this treatise deals with a great diversity of subjects, which are all treated as adequately as the limitations of space will allow. The longer chapters are devoted to the calcareous industry, clays, pottery, earthenware, porcelain, bricks, and glass. Methods of manufacture are in all cases discussed, with short directions for analysis and testing, and lists are given of the most important English and foreign books on the subjects, and the leading British journals are mentioned. The smaller industries included in the volume are of a more specialised nature, and information concerning them is not easy to get. Among them are disinfectants, permatite, thermit, enamels, thorium and cerium, radioactive substances, electric furnace products, and many others, and a large amount of useful information has been brought together by the writers who are responsible for the various sections.

The Journal of the Institute of Metals. Vol. xvii., No. 1, 1917. London: The Institute of Metals.

This number of the *Journal of the Institute of Metals* contains the report of the Annual General Meeting, which shows that great progress has been made by the Institute during the past year, both as regards number of members, financial position, and usefulness to the country in time of emergency. The papers read include among others a description of metal melting as practised at the Royal Mint, and others on metal melting by high pressure gas and other means. These, with the full reports of the discussions which took place after the papers had been read, make a contribution of considerable importance to the literature of the subject. The volume contains the usual abstracts of papers relating to the non-ferrous metals and the industries connected therewith, and a bibliography.

The Tokyo Imperial University Calendar, 1915-1916. Published Biennially by the University.

The calendar of the Tokyo Imperial University contains a historical account of the University, which consists of the six colleges of law, medicine, engineering, literature, science, and agriculture since its foundation in 1886. The general regulations which apply to all the colleges are given, with details of the courses of work provided and the syllabuses of the examinations for degrees, and it is clear that a high standard of work is expected from the students. The lists of publications, and of the contents of the journals of the colleges, show that a large amount of research work in all subjects is being done, and the University is evidently in a vigorous state of development. The calendar contains beautiful views of the colleges and plans of the gardens, &c.

THE CHEMICAL NEWS

Vol. CXVI., No. 3017.

WASAHBA WOOD.

By G. BURTON BAKER.

Mr. George W. Young, jun., of Des Moines, Iowa, while making a fishing pole of wasahba wood noticed that a resinous substance adhered to his hands. He attempted to remove the resin by washing with soap and water; his hands assumed a bright salmon pink or reddish colour. He concluded that this coloration was due to the alkali of the soap acting upon the gummy material of the wood.

Mr. Young then sent a few grms. of the sawdust to our laboratory to be further investigated. We shook up a little in water in a test-tube and it remained colourless. On adding any alkali solution to the test-tube, ammonia, sodium carbonate, potassium carbonate, caustic soda, or caustic potash, the red colour at once appeared. Any acid would make the contents of the tube colourless again. We also boiled some of the sawdust fifteen or twenty minutes in distilled water. On filtering the solution reacted with acids and alkalis as described in the foregoing.

H. P. Wells in his book entitled "Fly Rods and Fly Tackle" makes some observations on this wood as follows: "Beyond that bethabara or wasahba is a native of a hot climate and grows from three to three and a half feet in diameter, I have been able to acquire no certain information of its origin or growth. It is supposed to be like Greenheart, a native of British Guiana, and there known as wasabba, bethabara being a fancy name. It has the peculiarity of depositing a gummy substance on the edge of the plane blade, producing the effect of dulness, which must at short intervals be removed on the oil stone before the plane will resume its cut. When under the plane a yellow powder, closely resembling pulverised gamboge in appearance, is profusely deposited on the bench and tools as well as on the hands and person of the worker. This instantly turns a strong salmon colour in contact with soap and water, due doubtless to the action of the alkali in the former."

The specific gravity of the wood is 1·214. We found it difficult to work, as it is extremely hard, almost bony in texture. It is almost impossible to keep an edge on the tool with which it is worked.

We treated 5 grms. of the sawdust with 200 cc. of alcohol eight hours on the warm water-bath and filtered the extract. The solution was colourless, and resembled an alcoholic solution of phenolphthalein.

We next compared the alcoholic extract with a 1 per cent alcohol solution of phenolphthalein as follows (the alkalis and acids were used in diluted solutions):—

1. 2 cc. ammonia water, diluted to 50 cc. with water—

Phenolphthalein indicator required 25·8 cc. dilute HCl.
Wasabba wood " " 26·0 " "

2. 1 cc. KOH, diluted to 10 cc.—

Phenolphthalein indicator required 2·2 cc. HCl.
Wasabba wood " " 2·2 "

3. 1 cc. NaOH, diluted to 10 cc.—

Phenolphthalein indicator required 5·8 cc. HCl.
Wasabba wood " " 5·7 "

With sodium carbonate, ammonium carbonate, and potassium carbonate we could not secure concordant results. When the wood solution was used a larger amount of acid was necessary to produce the change than when phenolphthalein was the indicator.

We found that the red alkaline solution also serves as a dye, staining quite deeply a piece of white pine immersed in the liquid.

Cornell College, Mount Vernon, Iowa,
August 1, 1917.

COAL-TAR PITCH.

By JOHN MORRIS WEISS.

Much has been written on the subject of coal-tar pitch, largely in Germany, but most of the extant publications are very restricted in scope and consider only a method of testing, a specification for some particular purpose, or a description of a particular grade of material. To make a complete review of the literature would be a difficult task, and would be of little practical value for the purpose the writer has in mind. The object of this article is: (1) To treat in a rather general way the crude material for, and the manufacture of, coal-tar pitch; (2) to present the known physical and chemical characteristics of coal-tar pitch in a somewhat concise and definite form; (3) to consider the present uses of the material in industry—all from the point of view of United States practice.

Manufacture of Coal-tar Pitch.

Coal-tar pitch is the residual product from the distillation of coal tar, and tars are ordinarily distilled with the character of residue obtained as the primal object. The tar is taken in a horizontal, sometimes vertical, steel still fired by coal, oil, or gas (depending on local conditions), and distilled with air, steam, or mechanical stirring. Light oil and water are first separated, then carbolic oil, and finally creosote oil. The distillation is continued until the residue in the still is of the desired degree of consistency. Sometimes, where the pitch is being run very hard, anthracene oil is also separated toward the end of the creosote run, but this is exceptional, any anthracene oil obtained going for the most part along with the creosote oil. American practice has been very well set forth in an article by R. P. Perry, and the writer would refer to this paper for a more complete and exhaustive study of manufacturing methods (*Journ. Ind. Eng. Chem.*, 1913, v., 151: reprint from *8th Intern. Congr. Appl. Chem.*).

The characteristics of pitch are mainly dependent on two factors: The character of tar with which the still is charged, and the percentage of total distillate removed. The more oil removed the higher melting the pitch becomes. Factors such as type of still setting and method of running also affect the character of the pitch, but to a minor degree compared to the first two mentioned variants.

Crude coal-tars may vary widely, depending on the coal used for carbonisation, the type of installation in which the carbonisation takes place, and the degree of superheating to which the developing tar vapours have been subjected. In a paper by S. R. Church, read before the Southern Gas Association (*Gas Age*, May 15, 1913) there are given comparative analyses of a number of typical coal-tars, and it can be readily seen that there are wide differences in the characteristics of crude tars. (See Table A.).

These variations are in turn imparted to the pitch produced, and are largely dependent on the nature of the basic tar bitumens.

It may be set forth as an axiom that grades of pitch suitable for all purposes cannot be produced from a single source of tar. An admirable product for a particular purpose may be produced from each single tar, but in general it is safe to say that the best results are obtained by blending tars from various sources and altering the still mixtures to suit the purpose for which the residual pitch is designed.

Properties of Pitch.

In considering the properties of coal-tar pitches it may be said that all the testing methods, peculiar to the tar industry, have been given in detail by S. R. Church (*Jour. Ind. Eng. Chem.*, 1911, iii., 227; 1913, v., 195) and any references to specific properties not specially noted may be taken as determined by the methods given in this article.

Physical Properties.

1. *Melting Point.*—The term "melting point" is really a misnomer. Bitumens, such as pitch, which consist of a complex mixture of hydrocarbons cannot be said to have a melting point in the sense that this term is usually applied to pure compounds. When pitch is heated it gradually softens, passing by imperceptible degrees from the solid to the liquid phase, and the so-called melting point is merely an arbitrary figure taken for commercial purposes, and representing the temperature at which a cube of pitch softens sufficiently to drop from a wire, when heated at a prescribed rate and under rigidly controlled conditions.

The melting points of coal-tar pitch vary from 37·5° C. (100° F.) in water up to 174° C. (345° F.) in air. These are really the practical limits of manufacture. A material melting below 37·5° C. (100° F.) could hardly be called a pitch, but would rather come under the class of distilled tars, where the distillation has merely removed the water, light oil, and possibly a small portion of the carbolic oil fraction. Very hard pitches can be manufactured if desired, but ordinarily the hardest pitches may have an air melting point of not over 130° C. (266° F.).

2. *Specific Gravity.*—The specific gravities of coal-tar pitches vary from about 1·200 to 1·290 at a melting point of 37·5° C. (100° F.) and from 1·250 to 1·350 at a melting point of 88 to 93° C. (190-200° F.). Specific gravity is of comparatively little importance of itself. When an unknown pitch is examined the specific gravity determination may give an indication of adulteration with pitches from other sources, such as oil or water-gas tars. These are of lower specific gravity for the same melting point than coal-tar pitches, and any considerable adulteration will usually be reflected in the figure found.

3. *Effect of Heating.*—The effect of heating and melting of coal-tar pitch is at most a slight hardening due to volatilisation of oil. Trials on various grades at temperatures up to 205° C. (400° F.) showed only minor changes, and there was no evidence of cracking and decomposition. Pitches that have been hardened by frequent heating, unless badly overheated, can readily be brought back to the original consistency without altering their essential properties, by fluxing with a high boiling creosote oil.

4. *Solubility.*—Coal-tar pitches are soluble in benzol, carbon bisulphide, chloroform, carbon tetrachloride, and glacial acetic acid. Of course the free carbon does not dissolve, but can be brought into suspension by shaking. Coal-tar pitches are only partly soluble in petroleum naphthas, turpentine, grain alcohol, and wood alcohol, and any solution of coal-tar pitch in one of the materials which dissolve it, may be partially precipitated by the addition of an excess of one of the later named solvents. This is of considerable importance in the thinning of paints containing a coal-tar pitch base.

5. *Tenacity and Ductility.*—In the examination of bitumens these two properties are usually determined simultaneously. A cylinder of material of definite cross section is pulled apart under rigidly controlled conditions. The force necessary to do this is taken as a measure of the tenacity, and the lineal extension before rupture occurs as a measure of the ductility. These properties vary with the melting point of the pitch and the temperature at which the material is tested. To give detailed tests would take up much space and carry the writer outside the scope of this paper. The two properties are somewhat in inverse proportion. As tenacity increases, ductility tends to decrease. However, comparing coal-tar pitch with other bituminous materials of like tenacity, it is almost invariably of markedly greater ductility.

6. *Adhesion.*—This quality of pitch is its faculty to adhere to other materials, such as stone, felt, or wood, and it possesses this in a very high degree. This is of prime importance in many of the practical applications of pitch.

7. *Compressibility.*—It is well known that pitches will flow under pressure. Recent tests made in our laboratory by subjecting discs of bitumens to a smooth even pressure under rigidly controlled conditions of temperature have shown that coal-tar pitches show more compressibility at lower temperatures than other bitumens which apparently are less susceptible to changes of temperature as evidenced by the ordinary testing methods. Harder pitches will flow at temperatures considerably below their brittle points. They give under the smooth even pressure and do not splinter and crack as might be supposed.

8. *Electrical Properties.*—Tests made in our laboratories show the puncture voltage of pitch to be from 80,000 to over 100,000 volts per inch. Other tests showed the specific resistance to be so high that accurate measurements could not be obtained, the results varying from 168,000 megohms for 1 in. in thickness, to infinity.

Chemical Properties.

1. *Constitution.*—Very little is known of the actual nature of the compounds making up coal-tar pitches, but it is a generally accepted fact that these belong to the aromatic series. It is undoubted that some coal-tar pitches contain oxygenated hydrocarbons and all have some sulphur-containing bodies as part of their make-up. Nitrogen bodies are also present. It is possible that the nitrogen and oxygen contained in pitches are present in the form of higher homologues of the basic and phenolic bodies found in coal-tar creosote oil. C. R. Downs (*Jour. Ind. Eng. Chem.*, 1914, vi., 206) has published some ultimate analyses of briquette pitches in which one of the three pitches tested showed a notable amount of oxygen and all considerable quantities of nitrogen and sulphur. There is always a greater or lesser percentage of carbon, which is apparently not present in combination, but which is in the free state and is therefore called "free carbon." This is usually considered as the portion of the pitch insoluble in hot benzol and toluol. This insoluble matter is not pure carbon, but is very largely made up of this element. The nature of "free carbon" has been very extensively considered by the writer in a previous article (*Jour. Ind. Eng. Chem.*, 1914, vi., 279). The amount of free carbon in a pitch materially affects its physical properties, but no definite quantitative relation can be shown. It has been held by some that the free carbon not only affects the pitch *per se* but also by virtue of the nature of the bitumens which normally make up a low or a high carbon tar. The percentage of free carbon may vary from 10 to 50 per cent in various pitches. If a coal-tar pitch is ignited there is left but a small quantity of mineral ash, almost invariably under 1·0 per cent and usually under 0·2 per cent.

2. *Resistance to Acid.*—Concentrated nitric and sulphuric acids char and decompose coal-tar pitch. Dilute sulphuric acid up to a strength of 40° Bé. seem to have very little action. Dilute nitric acid has more effect, but weak solutions are very slow in disintegrating the material. Hydrochloric acid, concentrated or dilute, is very well resisted by coal-tar pitches, and heating the acid has little effect, provided the heat is not sufficient to melt the pitch. Glacial acetic acid dissolves coal-tar pitch, the solution being purely physical, more dilute solutions not affecting it.

3. *Resistance to Alkali.*—Most coal-tar pitches resist the action of caustic soda, caustic potash, lime, and ammonia. A very few, derived from tars of high phenoloid content, seem to be somewhat attacked by alkali, apparently due to the withdrawal of material soluble in this agent. For purposes requiring alkali resisting strength it is always possible to obtain a coal-tar pitch derived from tars which does not present this feature.

Table A.—*Analyses of Typical Tars.* (All tests on dry tar).

	Gas Retort.				Coke Oven.		
	Horizontal.		Inclined.	Vertical.	United Otto.	Semet-Solvay.	Koppers.
Sp. gr. at 15·5° C...	1·266	1·293	1·238	1·153	1·207	1·188	1·186
Free carbon (insoluble in C_6H_6)..	28·9	37·5	24·3	—	13·3	10·7	6·8
Specific viscosity (Engler at 100° C.) ..	21·8	30·0	14·9	2·1	3·4	3·0	2·1
Oil to soft pitch 60° C. m.p. (per cent by vol.)	13·2	—	14·3	28·8	21·2	21·8	35·3
Refractive index at 60° C. (taken on oil) ..	1·5932	—	1·5807	1·5755	1·5987	1·6122	1·6139
Sulphur residue (per cent taken on oil) ..	0·4	—	2·4	4·3	0	0	0
Tar acids (per cent taken on oil)	14·0	—	21·0	29·0	12·0	4·0	0
Pitch residue 60° C. m.p. (per cent by vol.)	86·8	—	85·7	71·2	78·8	78·2	64·7

4. *Air and Water.*—These two common reagents have practically no chemical effect on coal-tar pitches even after prolonged exposure. In the case of softer pitches exposed to the weather there is a gradual drying out of oil, and consequent hardening. In a paper by S. R. Church and the writer ("Experiments on Technical Bitumens, *Proc. A. S. T. M.*, 1915) the results of a year's exposure of pitches to atmospheric conditions are given, and it is shown that the alterations due to this exposure are of little importance.

5. *Other Chemicals.*—Coal-tar pitches have been shown to resist very well the action of concentrated bleaching powder solutions and solutions of many inorganic salts. In general it is a very resistant material so far as inorganic chemicals are concerned and is not readily oxidised.

In the paper by S. R. Church and the writer ("Experiments on Technical Bitumens," *Proc. A. S. T. M.*, 1915) experiments are presented which indicate that coal-tar pitch is affected to a lesser degree than bitumens from other sources by illuminating gas and gas drips. Illuminating gas from leaky mains frequently affects bituminous pavements, and both the gas itself and the liquid condensate have a serious effect on bituminous water-proofing below city streets.

6. *Combustibility.*—All coal-tar pitches are inflammable, but have such high flash points that risk from this source is comparatively small. Coal-tar pitches of 135° F. melting point have flash points of above 193° C. (380° F.) and fire points upwards of 243° C. (470° F.) when tested in an open dish on a sand bath. These high flash and fire points mean that there is a negligible risk in handling coal-tar pitches at the temperatures necessary for the application of the material.

Uses of Coal-tar Pitch.

1. *Roofing.*—The use of coal-tar pitch for roofing purposes is too well known to give it more than passing mention. A roof composed of coal-tar saturated felt with coal-tar pitch mopped between the plies and surfaced with coal-tar pitch and gravel or slag has stood the test of time, has been approved by the Underwriters' Laboratories as a fire-retardant roof, and has been adopted as a standard high-class roofing by architects and engineers throughout the United States. Its resistance to atmospheric conditions, its impermeability to water, and its adhesive qualities are of prime importance in this field.

2. *Waterproofing.*—Pitch is also used for underground waterproofing, on bridges, and in tunnels in very much the same way that it is used on roofs, that is, mopped between and on the surface of the plies of saturated felt. This use is also well known to architects and engineers, and coal-tar pitch waterproofing has been used widely with markedly favourable results. The qualities required here are about the same as for roofing purposes, but owing to the fact that such high temperatures are not generally encountered, a softer grade may be used. In this connection, the comparative resistance of coal-tar pitch to gas drips and illuminating gas is of considerable advantage.

3. *Paving.*—Coal-tar pitch has found wide application in the construction of pavements of various types. Probably the most important, although of comparatively recent development, is the use of very soft pitch as a binder in the construction of bituminous concrete and tar macadam roads. In brick pavements, granite block pavements, and wood block pavements, the proper grades of coal-tar pitch have found wide application, both as a filler beteen the blocks and as an expansion joint at the curb line. Many municipalities have issued specifications covering the quality of pitch to be used for these purposes. Pitch for this work is usually somewhat softer than that used for roofing materials.

The ability of pitch to give under pressure is of advantage, especially in its use as a filler in wood block pavement. With expansion of the blocks the pitch squeezes out and does not crack and allow moisture to penetrate the joints of the pavement. In general the adhesion of pitch to all sorts of surfaces makes it very valuable as a joint filler.

4. *Briquetting.*—The use of coal-tar pitch for briquetting fine coal or coke breeze has been developed abroad further than in the United States. There are two types of briquetting processes, one where the coal or coke is mixed hot with the pitch and the other in which the pitch is ground and mixed cold with the coal before pressing. In the first case a soft pitch is used which can be readily melted, and in the second process the pitch must be sufficiently hard to be readily pulverised. For this purpose the binding strength and waterproofing effect of the pitch makes it particularly advantageous.

5. *Core Compounds.*—This serves as an outlet for harder pitches than are used in briquetting work. Here the pitch is used as the binder for sand cores used in making castings of iron and steel. For this purpose a bituminous binder of low ash content is desirable and coal-tar pitch serves the purpose admirably.

6. *Paints and Protective Coatings.*—Solutions of coal-tar pitch in tar solvents comprise the main ingredients of the best tar paints. These are used for the protection of structural iron and steel, for waterproofing of interior walls, where it is desired to plaster directly over the paint, for acid-proofing and alkali-proofing paints and many other diverse uses. The reputation of tar paints has suffered much by poorly and improperly made materials. If properly compounded they are the equal if not the superior of many more expensive preparations for many purposes. That they can be completely ruined by thinning with non-compatible thinners is referred to in an earlier part of this paper.

7. *Miscellaneous Uses.*—Other uses which may be given passing mention are as a pipe dip, in the manufacture of ready roofings, as a cement in the joints of stoneware pipes, and as a constituent of various rubber and other compounds used for insulating purposes. Hard pitch is also used in the manufacture of electric light carbons and in the manufacture of "clay pigeons" or "flying targets." Of more recent development is the use of ground-hard pitch as a fuel in the same manner as powdered coal. This has been found of advantage in some metallurgical processes.

It is probable that an intimate knowledge of all the industries of the United States would develop many other important uses for this class of bitumens. Wherever a bituminous or plastic substance is used there is the possibility of the advantageous substitution of coal-tar pitch. Because of the great diversity in the nature of the crude tars it is possible to vary the characteristics of the residual pitches so as to make them cover a wide field of usefulness. In all chemical industry there is the possibility of its use, and it may be that only the unfamiliarity of many chemists and engineers with the real properties and characteristics of coal-tar pitch has prevented its wider application in our industrial establishments.—*Journal of Industrial and Engineering Chemistry*, viii., No. 9.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

By IRVING LANGMUIR.

(Continued from p. 136).

The Dissociation of Solids and the Kinetic Interpretation of the Phase Rule.

Some time ago it was pointed out to the writer by Mr. R. E. Wilson that a difficulty arises in the application of the kinetic theory to the dissociation of a substance such as calcium carbonate.

We may assume that in the equilibrium between calcium carbonate, calcium oxide, and carbon dioxide two opposing reactions are taking place at equal rates. Offhand, the most natural assumption in regard to these reactions would seem to be that the rate at which carbon dioxide is converted into carbonate is proportional to the pressure p of carbon dioxide and to the faction θ_1 of the surface which is covered by CaO. On the other hand, the rate of dissociation of the carbonate would be proportional to the faction θ_2 of the surface covered by $CaCO_3$.

If we equate these two rates we obtain for equilibrium—

$$p\theta_1 = K\theta_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (12),$$

where K is the equilibrium constant. This equation indicates that the pressure of the CO_2 should depend on the ratio between θ_2 and θ_1; in other words, it should depend on the relative proportions of the CaO and $CaCO_3$. This is contrary to fact. Evidently, therefore, we have made wrong assumptions regarding the mechanism of the reaction.

If we examine Equation 12 in the light of the Phase Rule we see that it would fit the facts well if there were a single solid phase of variable composition instead of two phases of constant composition. It would apply, for instance, to the dissociation of ferric oxide recently studied by Sosman and Hostetter (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 807), who found a "continuous series of solid solutions from Fe_2O_3 over to a point very near Fe_3O_4 if not over the entire range to Fe_3O_4."

Furthermore, when we analyse the assumptions made in the derivation of Equation 12 we readily see that they imply a solid solution phase. Thus it the rate of dissociation of $CaCO_3$ were proportional to the fraction of the surface covered by $CaCO_3$ it is evident that the surface would soon consist of CaO and $CaCO_3$ molecules distributed haphazard over the surface. This is exactly the kind of surface we should expect a solid solution to have.

The assumptions made above evidently are not consistent with the existence of separate phases of constant composition.

The Phase Rule, however, indicates that in the dissociation of calcium carbonate two solid phases, CaO and $CaCO_3$, are present together. In order that $CaCO_3$ may dissociate and form a phase of CaO (instead of a solid solution) it is *necessary that the reaction shall occur only at the boundary between two phases.*

Now, the CaO phase is generally so porous that CO_2 readily diffuses through it. We are then forced to conclude that the CO_2 in passing through the CaO does not react until it reaches the boundary of the $CaCO_3$ phase. In a sense, therefore, calcium carbonate must be looked upon as a catalyst for the reaction between calcium oxide and carbon dioxide.

From the kinetic point of view this must mean that carbon dioxide molecules are only absorbed to form calcium carbonate when by so doing they form a continuation of a calcium carbonate crystal already present.

It will be remembered that in the calcite crystal each carbon atom is surrounded by three systematically placed oxygen atoms. By examining a model of such a crystal it is readily seen that in the cleavage surfaces two of the oxygen atoms are probably close to the surface, while the third lies well under the surface. In the readjustment of the positions of the surface atoms which must occur when a cleavage surface is found, the atoms must tend to assume positions in which the forces between the atoms are balanced against one another. Such an arrangement may have a considerable degree of stability.

If we imagine one of the carbon atoms, with the pair of oxygen atoms adjacent to it to be removed from the surface, the symmetry of the arrangement of the surface atoms will be destroyed. This disturbance of the surface will certainly have no effect on the balance of forces holding the adjacent atoms. These atoms therefore will shift their positions. The neighbouring carbon atoms (with their oxygen atoms) will then be held to the surface by a force which is *different* from that obtaining before the first CO_2 was removed.

Now, if this force has been *strengthened* then the adjacent molecules of CO_2 will be less likely to leave than others further from the disturbed region. Therefore if the crystal is sufficiently heated, CO_2 would leave from all portions of the surface, and a *solid solution* of CaO in $CaCO_3$ would be found. On the other hand, if the removal of one CO_2 molecule sufficiently *weakens* the force by which the adjacent ones are held, then the CO_2 molecules will leave the surface only from positions adjacent to those from which they have already left. Under these conditions a separate phase of CaO would grow, starting from the point (nucleus) where the first CO_2 molecule left the surface.

We may therefore conclude, in the case of the dissociation of calcium carbonate, that the removal of a CO_2 molecule causes a weakening of the forces by which adjacent molecules are held, whereas in the case of the dissociation of ferric oxide the removal of an oxygen atom does not weaken the forces holding the adjacent oxygen atoms.

When a molecule of CO_2 strikes a surface of the CaO phase it presumably condenses, and may be held to the surface by forces no different in kind from those holding the calcite crystal together. However, if the removal of one CO_2 molecule from a surface weakens the forces by which adjacent ones are held, it is probable that the forces acting on a single CO_2 molecule in the midst of a surface of CaO would be extremely weak. Therefore the CO_2 molecule would remain on such a surface such a short time that the total number present in the CaO phase would not be of importance.

If, on the other hand, the forces holding the CO_2 molecule in the CaO phase were at all comparable with those acting at the boundary of the $CaCO_3$ phase, then we should have a variable phase consisting of a solid solution of CO_2 in CaO, together with a constant phase of $CaCO_3$.

It is readily seen that the mechanism we have assumed is capable of accounting for the different kinds of heterogeneous equilibria covered by the Phase Rule.

When there are two solid phases of constant composition and a gas, as in the dissociation of calcium carbonate, it follows directly from this mechanism that the pressure of the gas is dependent only on the temperature and not on the relative proportions of the phases.

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* From the *Journal of the American Chemical Society*, xxxviii, No. 11.

Thus the rate at which $CaCO_3$ dissociates is proportional to the number of $CaCO_3$ *groups adjacent to empty spaces*, while the rate at which $CaCO_3$ is formed is proportional to the pressure of CO_2 and to the number of *empty spaces adjacent to* $CaCO_3$ *groups*. Therefore the pressure must be constant at a given temperature.

(Note.—Since developing the above theory of the mechanism of such heterogeneous equilibria I have found that this subject has been treated by A. Thiel—*Sitzber. d. Ges. zur. Beforderung d. gesamt. Naturwiss. in Marburg*, 1913; *C. A.*, 1914, viii., 2284. Thiel accepts as an axiom the relation given by Equation 12, and hence concludes that θ_1/θ_2 is necessarily constant at a given temperature. This result is at complete variance with the theory given above, and, in the writer's opinion, is wholly unsupported by experimental evidence. In a subsequent paper the writer expects to discuss Thiel's theory in more detail).

This theory of the mechanism of heterogeneous equilibria appears to be particularly useful in accounting for various conditions not usually predicted by the Phase Rule.

Faraday noted a case that fully justifies the assumption that in some equilibria the reaction can occur only when the surface has been disturbed ("Experimental Researches," p. 109, Everyman's Library Edition). To quote from Faraday:—"As a curious illustration of the influences of mechanical forces over chemical affinity, I will quote the refusal of certain substances to effloresce when their surfaces are perfect, which yield immediately upon the surface being broken. If crystals of carbonate of soda, or phosphate of soda, or sulphate of soda having no part of their surfaces broken, be preserved from external violence, they will not effloresce. I have thus retained crystals of carbonate of soda perfectly transparent and unchanged from September, 1827, to January, 1833, and crystals of sulphate of soda from May, 1832, to the present time, November, 1833. If any part of the surface were scratched or broken then efflorescence began at that part, and covered the whole. The crystals were merely placed in evaporating basins and covered with paper."

It is well known that there is often great difficulty in removing the last traces of water of crystallisation from a substance even when the hydrate gives a definite vapour pressure. According to the theory given above, the velocity of the dissociation is proportional to the area of the boundary between the phases. This boundary will usually have its maximum extent when both phases are present in more or less equivalent amounts. But the great difficulty in removing the last traces is undoubtedly due to the formation of solid solutions (adsorption!). Let us consider a crystalline substance A B which dissociates into a solid phase A and a gas B. The dissociation of A B and the recombination of A with B takes place most easily at the boundary between the phases A B and A. However, in general, we should expect that A and B also combine throughout the phase A, but that this compound is more unstable, and therefore dissociates at a higher rate. The rate at which A and B combine in this way in a unit volume of the phase A will be proportional to the pressure p, while the rate at which it dissociates will be proportional to the concentration of B in A. By equating the two rates we see that the concentration of B in A should be proportional to the pressure of B.

There will therefore be the same kind of difficulty in removing the last trace of B from A as there is in producing a perfect vacuum.

The tendency of different substances to form these solid solutions will depend upon the extent to which the removal of one molecule of B from the phase A B affects the forces holding the adjacent molecules of B in A B.

It is a common experience that substances that are too thoroughly dehydrated are poor absorbers of moisture. A familiar example is over-burnt lime or plaster of paris. In some cases this phenomena may be due to a decrease in the porosity of the substance by sintering, but there is much evidence that this is not always the explanation.

According to the theory given above, the rate at which a partially dehydrated substance (which has a definite vapour pressure of moisture) will absorb moisture should be proportional to the extent of the boundary between the hydrated and dehydrated phases. According to this simple theory a thoroughly dehydrated substance should be incapable of absorbing any moisture. However, in general, there is no reason why vapour should not be slowly absorbed to form a solid solution even with a dehydrated substance. Gradually nuclei would develop in this solid solution and the hydrated phase would appear. The rate of absorption of moisture would then rapidly increase as the surface area of the hydrated phase grows.

Adsorption of Gases by Solids.

Unless the molecules of a gas which may strike a solid surface *all* rebound elastically there will necessarily be a higher concentration of molecules of the gas in the surface layer of the solid than in the body of the gas. If any molecules impinging on the surface are condensed a certain time interval must elapse before they can evaporate. This time lag will bring about the accumulation of molecules in the surface layer, and may thus be looked upon as the cause of adsorption.

In the condensation of a vapour we have seen that the collisions are wholly inelastic, so that every molecule striking the surface condenses.

The reasons that have led us to this conclusion apply with nearly equal weight to gas molecules of almost any kind striking any surface.

(Note.—There is good experimental evidence that this rule is not of universal application. When hydrogen molecules strike surfaces at room temperature apparently something like 80 per cent are diffusely reflected. This probably represents nearly the extreme case. However, even if 80 per cent of the molecules are reflected the adsorption of the gas on a surface is only five times less than it would be if none were reflected. Therefore every gas must be adsorbed to some extent on every surface. The evidence in regard to the reflection and condensation of gas molecules on surfaces is given in detail in a recent article—*Phys. Rev.*, 1916, viii., 149).

Let μ represent the number of grm.-molecules of gas striking each sq. cm. of surface per second. The quantity μ can be readily calculated from the pressure by means of the following equation, derived from Equation 4. (The nomenclature used here is the same as that employed in a recent paper on the dissociation of hydrogen, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 1148).

$$\mu = 43{\cdot}75 \times 10^{-6} \frac{p}{\sqrt{MT}} \quad . \quad . \quad . \quad . \quad (13).$$

The rate at which gas condenses on the surface will then be $\alpha\mu$, where α is a quantity usually very close to unity (never exceeding unity).

If the surface is that of a crystal there will be a definite number of spaces, N_0, on each sq. cm. of surface capable of holding adsorbed gas molecules. A greater number of gas molecules can only be adsorbed by the formation of additional layers of molecules. The forces acting between two layers of gas molecules will usually be very much less than those between the crystal surface and the first layer of molecules. The rate of evaporation in the second layer will therefore generally be so much more rapid than in the first that the number of molecules in the second layer will be negligible. (The detailed development of this theory of adsorption, taking into account the evaporation from each of the layers and other complicating factors, will be published as Part II. of the paper in the *Phys. Rev.* References to previous literature on the subject will be given at that time. The present paper deals principally with the chemical aspects of the theory). When a gas molecule strikes a portion of the surface already covered it thus evaporates so quickly that in effect it is equivalent to a reflection. Therefore the rate of condensation of the gas on the crystal surface is $\alpha\theta\mu$, where θ represents the fraction of the surface which is bare. Similarly, the rate of evaporation of the molecules from the surface is equal to $\nu_1\theta_1$ where ν_1 is the rate at which the gas would evaporate if the surface were completely covered, and θ_1 is the fraction actually covered by the adsorbed molecules. When a gas is in equilibrium with a solid surface these two rates must be equal, so we have—

$$a\theta\mu = \nu_1\theta_1 \quad . \quad . \quad . \quad . \quad (14).$$

Furthermore—

$$\theta + \theta_1 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (15).$$

Whence—

$$\theta_1 = \frac{a\mu}{\nu_1 + a\mu} \quad . \quad . \quad . \quad . \quad . \quad . \quad (16).$$

The quantity θ_1 is a measure of the amount of gas adsorbed. It should be noted that for low gas pressures the amount of adsorbed gas is proportional to the pressure, but as the pressure increases θ_1 increases more slowly, and finally the surface becomes saturated ($\theta_1 = 1$). These relations are in good qualitative agreement with known facts.

(Note.—Equation 16 gives the amount of adsorption on a plane crystal surface. No reliable quantitative experimental data seem to be available for the adsorption of gases on such surfaces. The writer is therefore undertaking measurements of this kind at present, and will report the results at a later date. The theoretical reasons for believing that Equation 16 is not quantitatively applicable to adsorption by porous bodies, such as charcoal, will be discussed further on in this paper).

Equation 16 indicates that at low temperatures (small value of ν_1) the amount of adsorption should be large and nearly independent of the pressure, while at higher temperatures (large value of ν_1) the amount of adsorption should be small, and should be proportional to the pressure even at high pressures. These deductions also are in qualitative accord with experimental facts.

From Equation 16 we see that the tendency of a gas to be adsorbed on a surface is determined by ν_1, the rate of evaporation from the surface. This quantity in turn depends on the magnitude of the forces acting between the atoms of the crystal and those of the adsorbed substance.

These forces will be of the same nature as those which hold solid bodies together. We may therefore profitably look upon them as chemical forces, and apply our knowledge of the chemical properties in studying the phenomena of adsorption.

With a gas such as nitrogen, in which the atoms are mutually very thoroughly saturated, we know that there is only a weak field of force around the molecules. When a nitrogen molecule strikes a surface the forces holding it are only those due to weak secondary valence. It is to be expected, however, in general, that the forces by which molecules or atoms may be held on a surface should show, for different substances, as great a range of intensity as is observed in the case of the forces acting inside of solid bodies.

Solid nitrogen is held together by comparatively weak forces, while the forces in solid carbon or tungsten are among the most powerful known. In the case of adsorbed films the magnitude of the forces should vary all the way from the weak forces observed with adsorbed nitrogen (or better helium) up to forces which are as intense as those holding together the atoms of the most stable chemical compounds. Just as we find either secondary or primary valencies active between atoms in solids so should we expect both kinds of valence to take part in the formation of adsorbed films. When we thus speak of adsorption as a chemical phenomena it should be remembered that we must also regard evaporation and condensation in general as chemical phenomena. The point to be emphasised is that there is no real distinction between these so-called physical phenomena and true chemical phenomena, except that, in general, the "physical" phenomena depend on secondary valence rather than primary. Since, however, chemical phenomena involve secondary valence as well as primary, it seems best to classify all such phenomena as chemical. By so doing we do not in any way fail to recognise the close relationship between evaporation, condensation, and the adsorption of the relatively inert gases.

This chemical theory of adsorption has received striking confirmation by many experiments in the research laboratory of the General Electric Company, Schenectady, N.Y.

Experimental Evidence that Adsorption is a Chemical Phenomena.—It has been found that atomic hydrogen, produced by heating a metallic wire in dry hydrogen at very low pressures, has a remarkable tendency to be adsorbed on surfaces (Langmuir, *Journ. Am. Chem. Soc.*, 1912, xxxiv., 1310). According to the usual "physical" theory of adsorption by which the adsorbed film is assumed to be a layer of highly compressed gas we should expect that a gas of such low density as atomic hydrogen would be only slightly adsorbed. Furthermore, we should expect that an adsorption film in high vacuum would very rapidly reach equilibrium with its surroundings.

The experiments showed, however, that even in the highest vacuum quantities of hydrogen as large as 0·01 to 0·03 cubic mm. (at atmospheric pressure) per sq. cm., could be adsorbed on cold glass, and that this adsorbed film was remarkably stable, being able to remain unchanged on the surface for several days. To account for these adsorption phenomena it was suggested in 1912 (*loc. cit.*, p. 1313) that "perhaps the unsaturated chemical affinity of the atomic hydrogen gives it unusual tendencies to be adsorbed on surfaces." It was observed that the amount of atomic hydrogen which could accumulate on a given surface was strictly limited, and it was shown that this was not due to a balance between the rate at which atomic hydrogen spontaneously escaped from the surface and the rate at which it was deposited. On the contrary it was shown that the amount was limited because, after a certain amount of atomic hydrogen was present on the surface, fresh atoms of hydrogen striking the surface combined with those already present, and thus removed them.

It is interesting to compare the amount of atomic hydrogen adsorbed on the glass with the amount necessary to form a layer one atom deep. If we take the diameter of the hydrogen atom to be the same as that of the molecule, namely, about $2·5 \times 10^{-8}$ cm., we may conclude that the number of hydrogen atoms per sq. cm. needed to form a layer one atom deep is about $1·6 \times 10^{15}$. This corresponds to 0·032 cubic mm. of molecular hydrogen at 20° and one megabar pressure. The maximum amounts of atomic hydrogen which were found adsorbed on glass surfaces were of this same order of magnitude (0·01 to 0·03 cubic mm. per sq. cm.).

In a subsequent paper (Freeman, *Journ. Am. Chem. Soc.*, 1913, xxxv., 927) it was shown that atomic hydrogen could diffuse several feet through glass tubes at room temperature, but could not pass even through a short tube cooled in liquid air. This may be taken as evidence that practically all hydrogen atoms striking a cold glass surface condense. With the glass cooled by liquid air these atoms do not evaporate at a perceptible rate, but from glass at room temperature they evaporate sufficiently rapidly to permit the passage of the atomic hydrogen through a long tube.

The experiments with atomic hydrogen thus furnish evidence that:—

1. The adsorption is determined by chemical affinity,
2. The adsorbed layer does not exceed one atom in thickness.
3. Hydrogen atoms striking glass surfaces are not reflected.

Similar evidence has been obtained from experiments with tungsten filaments in oxygen at low pressures. It was shown that 15 per cent of all oxygen molecules striking a tungsten filament at 2770° K. react with it to form WO_3 (Langmuir, *Journ. Am. Chem. Soc.*, 1913, xxxv., 105). More recent experiments (as yet unpublished have shown that this coefficient continues to increase at higher temperatures, so that at 3300° K. about 50 per cent of all the oxygen molecules which strike the filament react with it to form WO_3. Since there are three atoms of oxygen in WO_3, and only two in the oxygen molecule, it is evident that *at least* one-half of the tungsten surface even at 3300° K. must be covered with oxygen in some form. When we consider that the pressure of oxygen in these experiments was usually not over 5 bars we realise the extraordinary stability of the film, and are thus led to believe that the oxygen atoms are held by chemical forces to the tungsten atoms which form the lattice structure of the tungsten crystals.

It is very evident that the adsorbed film does not consist of tungsten oxide, WO_3, since this substance distils very rapidly from the filament even at temperatures as low as 1200° K. The film has no perceptible effect on the optical properties of the tungsten surface, since low pressures of oxygen do not cause any perceptible change in the characteristics (volts, ampères, candle-power) of the tungsten filament.

The existence of this oxygen layer on a tungsten filament in oxygen at low pressure shows itself in many other ways. Thus a pressure of 0·001 bar of oxygen lowers the electron emission from a tungsten filament at 1800° to a very small fraction of its normal value. Even more striking evidence has been recently found in connection with experiments (as yet unpublished) with tungsten filaments in mixtures of various gases at low pressures. It is found that a tungsten filament at 1500° K. in a mixture of oxygen and hydrogen reacts with the oxygen exactly as if no hydrogen were present. While this oxidation of the tungsten is going on, none of the hydrogen reacts with the oxygen, and the hydrogen does not reduce any of the tungsten oxide formed, nor is any atomic hydrogen produced. (This is especially remarkable since WO_3 is readily reduced by hydrogen at atmospheric pressure at temperatures as low as 500°). However, after all of the oxygen has been used up (partial pressure reduced to less than 0·01 bar) the hydrogen *suddenly* begins to disappear by being dissociated into atoms which then react with the WO_3 previously deposited on the bulb.

Simultaneous measurements of the electron emission show that this emission increases suddenly at the same moment at which the hydrogen begins to disappear. This experiment proves:—

1. That in presence of even 0·01 bar of oxygen the surface of the tungsten at 1500° K. is practically completely covered with oxygen.
2. That this layer of oxygen will not react with hydrogen even at 1500° K.
3. That such a layer of oxygen prevents the formation of atomic hydrogen.
4. That the decrease in electron emission produced by oxygen is due to the same cause as that which prevents the dissociation of hydrogen.

It is very evident from this work that the oxygen layer has totally different properties from those we should expect, either with a layer of oxide or a film of highly compressed gas. The facts are in good accord, however, with the theory that the oxygen atoms are chemically combined with the tungsten atoms. From this viewpoint the two primary valencies of the oxygen are turned downwards, and are saturated by the tungsten so that a hydrogen molecule striking the surface cannot react with the oxygen and cannot come in contact with the tungsten. The hexavalent tungsten atoms, on the other hand, are not saturated by the oxygen, so that they are held firmly to the underlying layer of tungsten atoms. Only when the tungsten atoms on the surface become saturated by taking up two other oxygen atoms do they cease to be held to the other tungsten atoms and thus evaporate off as WO_3.

(Note.—The fact that the tungsten atoms leave the surface only after they have been completely saturated chemically seems to be an example of a general tendency. Thus when tungsten is heated in chlorine at very low pressures the hexachloride, WCl_6, only is formed, although several stable lower chlorides of tungsten exist. When Pt is heated at high temperatures in oxygen at moderate pressures the oxide, PtO_2, distils from the surface, while an osmium filament in oxygen at low pressures gives OsO_4. Molybdenum in oxygen gives only MoO_3).

The stability of the oxygen layer is due to the strength of the chemical union between oxygen and tungsten atoms, which results in a very slow rate of evaporation of the oxygen atoms from the surface.

(To be continued).

FOOD PRODUCTION PROGRAMME FOR 1918.*

Reference has been made in some newspapers to an announcement which it is stated has been issued by the Food Production Department that five million additional acres are to be under corn and other crops in 1918. No such announcement has been issued by the Department. It is possible, however, that the error is due to a misunderstanding of a brief summary which has been published of the 1918 Tillage Programme for England and Wales. This summary is as follows:—

"As compared with 1916—
1. To increase the area under Corn by 2,600,000 acres
2. To increase the area under Potatoes and Mangolds by 400,000 acres.
3. To increase the Arable Land by 2,000,000 acres."

Apparently the three areas mentioned in the above statement have been added together, producing a total which is obviously incorrect. The Department's Programme, already published, aims at securing three million additional acres under corn, potatoes, and mangolds. This additional acreage they hope to obtain by breaking up two million acres of grass land (not five million as stated), and by converting one million acres now devoted to crops of less national importance (*e.g.*, mustard for seed, hops, &c.) to food crops.

THE PRICES OF SUPERPHOSPHATE.*

The War Cabinet has fixed minimum prices for the sale of superphosphate in the United Kingdom on the basis of a delivered price of £6 5s. for 28 per cent grade if delivered in December with a reduction of one shilling per month before December and 1s. per month rise from January until May, 1918.

Thirty per cent superphosphate costs £6 10s. From 30 per cent downwards there is a reduction of 2s. 6d. per ton for each complete unit; from 30 per cent upwards an extra of 4s. for each complete unit. The prices are for net prompt cash, in makers' or vendors' bags, delivered by rail or water to consumer's nearest railway station or wharf.

An Order to this effect has been issued by the Ministry of Munitions, and a circular explaining the provisions of the Order can be obtained from the Food Production Department. The principal provisions of the Order are summarised below:—

1. *Prices for Deliveries by Rail or Water from Makers' Works.*—Superphosphate is to be sold by makers in lots of 2 tons and upwards delivered by rail or water at consumer's nearest railway station or wharf at the prices specified in the schedule given below.

2. *Discount to Dealers.*—Manure mixers, agricultural merchants and dealers, and co-operative societies registered under the Friendly Societies Acts are to be allowed a discount on the Scheduled prices of 2s. 6d. per ton on purchases of two tons and upwards.

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* From the Food Production Department.

3. *Prices for Deliveries by Road in Consumers' Carts.*—Where the consumer takes delivery from makers' works into his own carts or wagons for conveyance direct by road to his premises in lots of two tons and upwards a deduction of 10s. per ton is to be made from the scheduled prices. It must be understood that makers are under no obligation to sell on these terms, as their ability to deliver into farmers' carts necessarily depends on the orders in hand for delivery by rail, the stocks available for the fulfilment of orders for future delivery, and the loading facilities at the works. Makers are not required to incur any expense or to provide labour for loading.

4. *Prices for Sales to Channel Islands.*—In the case of sales of lots of two tons and upwards for shipment to the Channel Islands superphosphate is to be delivered f.o.b. at port of shipment at the scheduled prices.

5. *Prices for Sale from Store, Shop, and Warehouse.*—Where superphosphate is sold for delivery ex vendor's store or shop (but not ex maker's works), or ex warehouse, railway goods yard, or public wharf the following additional amounts may be charged:—

4 tons and over	5s. per ton.
1 ton and over, but less than 4 tons ..	10s. per ton.
2 cwts. and over, but less than 1 ton ..	1s. per cwt.
Less than 2 cwts.	2s. per cwt.

(Additional to the prices shown in the schedule).

These additional prices do not apply to sales of more than 1 ton for delivery ex railway goods yard or public wharf.

6. *Additional Allowance for Delivery by Road ex Store.*—In the case of sales for delivery by road to consumer's premises from maker's works or vendor's store or shop, or from warehouse, railway goods yard, or public wharf, cartage or haulage at local rates may be charged in addition to the prices specified in paragraph 5.

7. The prices referred to above are in all cases net prompt cash prices for superphosphate in maker's or vendor's bags. Where credit is given to the purchaser a reasonable extra charge may be made, provided that a price for net prompt cash is quoted on the invoice and does not exceed the maximum price authorised. If purchaser's bags are used a reasonable allowance is to be made.

8. The above prices apply to superphosphate of lime manufactured from mineral phosphate, but do not apply to basic superphosphate, bone superphosphate, dissolved bones, bone meal, or bone compound, guanos, or compound manures.

Distribution of Superphosphate.

9. It is hoped that the output of superphosphate will be sufficient to meet the demand. It is, however, very desirable that orders should be placed at once, and with this object the prices given in the schedule below have been arranged in such a way as to allow a small rebate for orders placed for delivery before December, after which month prices rise by one shilling per ton per month.

10. It has been arranged that makers will accept orders for delivery in any specified month up to the limit of their output in that month, in the order in which they are received. Deliveries which cannot be made in the month promised will be made as soon as possible thereafter, but at the price of the month for which they were promised. If an order is accepted for delivery as soon as possible without any month being specified the price will be according to the month in which delivery is made.

11. Farmers should place their orders with the maker, dealer, or agent with whom they are accustomed to deal, and take delivery at the earliest possible date. In the event of any difficulty in obtaining supplies application should be made to the Secretary, Phosphates and Potash Distribution Committee, 72, Victoria Street, London, S.W. 1.

12. Merchants of repute are being recognised by the Agricultural Executive Committees in England and Wales as roved agents for the sale of fertilisers, and the names of these merchants, as well as any other information issued, can be obtained on application from the Food Production Department, 72, Victoria Street, London, S.W. 1.

THE POTASH INDUSTRY OF CANADA.

The chemist of to-day who thinks of the production of potash in terms of the output of Stassfurt will be surprised to learn that at the middle of the last century between two-thirds and three-fourths of the world's product of potash came from Canada. Regarding this product as a Canadian industry, it will be equally surprising to learn that for many years the export of pot-ash and pearl-ash ranked next to lumber in the shipment of forest products to other countries. In the fifties the export of potash and pearl-ash from Upper and Lower Canada for several years exceeded a million dollars in value per year, and a million dollars was a big sum to the Canadians of those days. It was very important to the individual settler in the first half of the last century, because it was the one product of all his varied labours that could be depended on for ready money. It was paid for in cash, whereas most of his other earnings and crops were traded for groceries, drygoods, and implements. His wool went to the custom woollen mill and came back in cloth or in roll cards for the settler's wife to spin; the wheat went to the grist mill and came back largely in flour and feed, and butter and home made cheese came back in other groceries; but potash always came back in real money.

In many parts of the country the manufacture of pot and pearl ash became a specialised industry carried on all the year round. Men were employed in going through the settlements, collecting the ashes saved by the farmer who burnt his timber, not more for the sake of clearing the land than for the sake of the money obtained from the sale of the ashes. Many farmers had their own pots and converted their wood into potash, while every new settlement established an "ashery" in which both pot and pearl ash would be made, from ashes hauled in from neighbouring clearings. In 1851 there were 237 asheries in Upper and Lower Canada (Ontario and Quebec). In 1871 there were 519; but by 1891 these had dwindled to 128 for the whole of Canada, and now the industry on this plan is almost extinct. However, during the last few years up to the outbreak of war the exports of potash from Canada averaged about 500 barrels per year, valued at nearly 25,000 dols., or 50 dols. per barrel. While during the last century Canada was the world's chief producer of potash, she has now become an importer, the imports before the war averaging about 250,000 pounds, valued at about 9000 dols. During the first half of the last century Great Britain was the world's chief market for potash, and the pre-eminence of Canada in this industry is indicated by the fact that in 1831, for example, Great Britain imported potash and pearlash to the amount of 228,757 cwt., of which 169,891 cwt. came from British America, 15,835 cwt. from the United States, and the balance from Russia and Poland.

Most of this output was exported direct to England, the shipments by the St. Lawrence often amounting to more than a million dollars a year. Considerable quantities went out from Upper Canada by way of Buffalo, and frequent schooner loads came down the Grand River every season for delivery here to New York and New England ports. Potash entered England free from Canada, but until free trade was adopted there was a duty on American potash of 6s. per cwt. The price in England in the thirties was about £1 5s. 6d. for pearl-ash, and £1 4s. 6d. for potash.

A Canadian work of reference, published in 1863 and edited by Prof. Hind, the geologist, and T. C. Keefer, the well-known civil engineer, described the process of manufacture in Canada as follows:—"The produce of the forest of most importance next to lumber has always been pot and pearl ashes. Potashes are made from the crude ashes by dissolving the soluble portion of the ashes with water, evaporating to dryness and fusing at a red heat into a compact mass, which although grey on the outside is pink within. Pearl-ash is made by calcining potashes upon a reverberatory hearth until the carbon and much of the sulphur are dissipated. Water is then added and a lye formed which, when evaporated to dryness, yields the pearl-ash of commerce. Canadian potashes contain on an average 60 per cent. of carbonate ot potassa. Pearl-ash contains generally about 50 per cent. of caustic potassa."

In the fifties the cost ot manufacturing was estimated at 10 dols. per barrel when the selling price in Montreal was 40 dols., and, therefore, the manufacture of potash was strongly urged as an industry whose profits were certain and permanent. One advocate stated the case thus:—"No one item of our available exports is of higher importance than potashes and pearl ashes. In a country where it is necessary that vast tracts of wild land should be cleared,—land covered with a heavy growth of timber, useless in the main for other purposes than the manufacture of ashes,—this needs only to be looked at to discover its utility."

To-day the forests of Ontario are worth for other industries twenty to thirty times the value of their potash, and Canadian lumbermen will learn with vexation that in the tract referred to,—that is, the region lying between London and Detroit,—the timber spoken of as worthless for any use other than potash, comprised Birch, Beech, Oak, Pine, Maple, Elm, Cherry, Hickory, Ironwood, Black Walnut, and many other woods which are now rare and costly.

With the clearing of the forests of Eastern Canada the potash industry declined, and this decline was hastened by the opening of the great deposits of Stassfurt, Germany. But since the war has cut off the German supply, and since Great Britain, the United States, Canada, and the other British Dominions seem to have determined that they shall be self-dependent as to such products, the present problem is to discover new sources of potash and nitrates,—both essential in the field of agriculture, as well as in chemistry. While it is true that in Canada and the United States there has been throughout the last hundred years an enormous waste of material in almost every industry, and none of greater enormity than in wood, yet all that can now be saved of the remnants of our forests will never restore the potash industry on the old basis. It will be interesting to note that the Town of New Toronto is now installing, under the supervision of its engineers, Messrs. James, Loudon, and Hertzberg, a system of incineration for the treatment of garbage, by which potash is recovered to the value of 7 dols. to 10 dols. per ton. The incinerator is designed by the Reid Products Company of Toronto, who have installed plants in several towns and have designed a small type for private works. Of the latter, thirty-eight were installed at the military grounds at Camp Borden. Such endeavours to utilise the waste of cities should be encouraged, but, at best, they can only yield a fraction of the potash required.

There is still, however, a source of potash in the felspar rocks of America, vaster than has ever been exploited from wood, and without doubt chemistry will sooner or later solve the problem of profitably extracting it. There are millions of tons of felspar rock in Canada, and in some sections the potash contents run from 10 to 14 per cent.

The cost of extracting the potash must be reduced by using other elements of the rock as by-products, and aluminium compounds, porcelain, and Portland cement can do this in some districts. The making of potash as a by-product of the cement industry is now much talked of in Canada, but the claims made for the processes have not yet been demonstrated on a commercial scale; and, in any case, the output in this class is necessarily restricted to the market obtainable for the cement.

Generally speaking, the areas of felspar rock in the northern half of this continent yield a porcelain that is whiter and freer from iron, and for this reason large quantities of Canadian felspar are shipped to the United States, ranging from 11,000 to 18,000 tons per year,—to be used in the pottery and porcelain industries, and for the manufacture of artificial teeth, &c., and there would seem to be room for further development of such industries and for aluminium in both countries in combination with potash production. When the nickel areas of Sudbury were opened up, the peculiar combinations of the ore presented a knotty problem to be worked out, but patience, skill, and money solved every difficulty, with the result that to-day the Sudbury district now supplies 80 per cent of the nickel output of the world. There is every reason why all obstacles will be overcome likewise in the production of potash, and if so, the primacy in the manufacture of this most essential material will be restored to America.—*The Canadian Chemical Journal*, i., No. 3.

FEEDING OUR FOOD.*

The present effect of Mr. Lloyd George's recent speech and of Mr. Kennedy Jones's explanation of his resignation would seem to be beyond doubt, at least so far as my recent observation in Yorkshire shows. The Premier, it will be remembered, told us about our stocks of food and the prospects of the harvest. Mr. Kennedy Jones, in an utterance which must surely vie for mischievousness with anything said, even by our politicians, in the last three years, told us that he resigned his post as Director-General of Food Economy because his work was done and there was no further need for his continuance of it. Meanwhile there has been the weather; the Germans have more U-boats and we fewer ships every week; and there is next spring to fend for. But in this part of the country people are eating steadily and hard, posters on food economy are conspicuously absent to a Londoner's eyes, and large numbers of men with no complementary pretensions in speech or appearance show themselves in the evening with the full allowance of good food upon their shirts. This is pure swank; they have a chance of being seen in evening dress and they take it, excellent edible starch being accordingly plastered to make a bourgeois holiday. To anyone who knows the elements of the facts which are before us, this nightly spectacle and the grossly generous eating during the day and all day are shameful and ominous and alarming. Hence what follows. We import and grow our food. It is to be presumed that the Shipping Controller has physiological advisers who prepare for him complete tables showing a scale of possible foodstuffs according to the number of calories, let us say, that they furnish per unit of freight space. Obviously, to take instances at random, it is sound shipping economy to import flour rather than grain, and chilled beef rather than fodder.

As for the food we grow, there is a Food Production Department. The Food Controller, we note, is at the mercy of the Ministries of Shipping and Agriculture. If, for instance, these Ministries imagine certain things to be foods which are not foods but drugs or poisons—such as hops, tobacco, mustard, or what not—the Ministry of Food will have so much less food to administer. Thus one learns from the latest agricultural returns that mustard has lost the large increase recorded last year and the area is now below that of 1915. Mustard is an admirable emetic, and is also largely used to increase our already excessive, and now actually dangerous, consumption of beef. For which of these purposes it was so extensively grown last year I fail to surmise; but no one can fail to see that the Board of Agriculture and the Food Production Department must imperatively employ, if they are to do their best for us, an analogous criterion to that required by Sir Joseph Maclay; how many calories per month or per annum per acre will a given plant yield? Why, for instance, has the area under turnips increased this year? And is there another country on the face of the earth which shares our inane partiality for this inane root? Or to whom could we furnish an intelligible reason for competitions about vegetable marrows when food supply may determine the fate of freedom?

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* From *The New Statesman*, September 15, 1917.

The British Association, by an ignominious abdication, ill-timed as such could never have been in the three-quarters of a century or so of its fine history, has decided not to meet this year—when scientific discussion of such questions as I have tried to deal with in these columns during the war was never so much needed. One can hear the contemptuous laughter of Germany at this pathognomonic symptom of our national disease. "The Republic has no need of chemists," said the mob who struck off the marvellous head of the aristocrat Lavoisier; and that is the sentiment of our aristocracy and our mob alike to-day. Consider, for instance, the shouting ignorance on every side, indignantly attacking the Ministry of Food in the matter of beef, though for sixpence anyone may obtain the invaluable pamphlet by Prof. Wood,[*] already briefly referred to elsewhere in this journal, and learn forthwith that the growth of beef is, in fact, the wholesale destruction of food, just as brewing is. There is food in beef and there is food in beer; but the production of either is nevertheless the destruction of food, and must be drastically controlled accordingly. This is highly disconcerting to what George Meredith called "the religion of the Englishman, his beef, his beer, his pew in eternity," but famine would be more disconcerting still, compromising his hold on his pew in time—which touches him much more nearly.

We have just put upon the Statute Book a Corn Production Act. What would any intelligent German or American, knowing our conditions, expect to be the first provision of such an Act? *Fixed nitrogen* is the answer. Needless to say, the term is merely "blokes'" jargon to those who framed and those who discussed the Act. But if we are to produce corn we must feed it. Not even the green plant can create energy. It transforms the solar energy most wonderfully, but that is not enough. Given sun and air and seed and water, we must provide oil, or, more precisely, *food* for the seed and the plant. Just as we animals need, primarily, the proteins which the plant alone can make for us, with their nitrogen not only fixed but highly organised so the plant, before us, needs primarily such compounds as nitrates and salts of ammonium, containing nitrogen fixed in forms too simple for our bodies to employ, but exactly fitted for the plant's more skilful anabolic powers.

Hitherto we have relied upon the nitrate fields of Chile and upon our ships. The war, demanding nitrogenous explosives, has immensely increased our dependence upon those nitrate fields. Some of our leaders suppose that, by blockading Germany, so that no nitrates could reach her, we should soon make a famine both of food for men and food for guns. Meanwhile, Germany proceeded to fix ever-increasing quantities of nitrogen from her own air; and in recent weeks her agents have been fomenting strikes at the nitrate fields and ports, well knowing our dependence thereon and our criminal neglect of nitrogen fixation at home, whilst we boast of our blockade.

This is no German secret, or German invention. Germany does not invent; invention being, indeed, somewhat of the nature of an impropriety in a State where obedience to the powers that be is the whole duty of the citizen. But she appreciates and adopts and improves. The man who first drew attention to the facts upon which the continued existence of civilisation depends was an Englishman, now the doyen of all chemists. More than once during the war I have here attempted to interest those who control our fate in the propositions which Sir William Crookes laid down in his Presidential Address to the British Association some twenty years ago. I commented upon the disgraceful fact that his book, founded thereon, and called "The Wheat Problem," has been out of print for many years;[*] and, though the late Prof. Silvanus Thompson showed us the electrical production of nitrates from the air at the Royal Institute a decade or more ago, Sir William and he might never have existed for all that has been done for our protection in these terrible times.

However, my first article was read to some purpose in at least one instance. Messrs. Longmans now have in hand the MSS. of a new edition of this book, prepared by Sir William Crookes himself, and the volume will shortly appear, under very high and appropriate auspices indeed. I earnestly hope that arrangements are now being made for an American edition. This would do something to raise British credit for intelligence on the other side of the Atlantic, where our methods have been watched with such complacent pity in recent years. After all, we do produce the great men, as we have done for centuries past. It will be well to remind our welcome new Allies that our chemists were in the van in this respect decades ago and are still alive and alert. A further reason for the speedy publication of an American edition is to be found in the recent statement made by Dr. Allerton Cushman in a paper before the Franklin Institute, to the effect that the United States Congress has voted a hundred million dollars for the fixation of atmospheric nitrogen.

With all my heart I congratulate our illustrious veteran, not merely that he should have lived to see the absolute fulfilment of his predictions, made now so long ago, and laughed at so freely by fools then, but especially that he should have been able, in this present year 1917, to have rewritten his book and given us, not merely the new edition I asked for, but what will, I doubt not, be in effect a new book, upon the teaching of which we had better act forthwith. For, indeed, why should we not fix our own nitrogen as Germany fixes hers to our confusion, and as the United States are about to do? It has been said that the electrical method is all very well for countries rich in water-power, as we are not. But it appears that this method, which had its origin in Scandinavia, has been largely superseded by another, dependent upon an entirely different principle and lucidly described by Prof. Findlay in a recent paper in this place. This new method the Germans are now employing. If Corn Production and the production of explosives be our immediate need, should we not proceed to fix our own nitrogen forthwith?

There is still a vocal school to return a negative, arguing that the less we hear about this new-fangled nonsense the better, and that farmyard manure will always be the best, as it was in the beginning. A recent letter in the *Times*, from a correspondent who is subsequently referred to as an authority by a leading article in that journal, indicates the survival of a state of agricultural opinion corresponding to the military opinion which is always eagerly awaiting the moment when our cavalry shall break through, round up and capture the Germany Army. The argument is that there will be grave reduction in our supplies of corn unless the Food Controller fixes such prices for beef as will enable the producer to feed and fatten it as usual. The whole argument rests upon the ignorant view of farmyard manure, for which we are required to destroy fabulous quantities of food in order to maintain the life of oxen, whose carcases will be all that we have left in the end thereof. Just consider these two sentences from the letter in question: "It is quite clear that the Food Controller has the power utterly to frustrate any attempt to increase the food production of the country. The earth may be scratched, pasture ploughed up and destroyed, but so far as yield is concerned there will be nothing but disappointment unless stock are fed in the winter." And then read

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[*] "The National Food Supply in Peace and War," by T. B. Wood, M.A., Professor of Agriculture in the University of Cambridge. Cambridge University Press, 6d. net.

[*] The writer is under a misapprehension; the work has never been out of print, and is still on sale at the Chemical News Office.—Ed. C. N.].

Prof. Wood on "Wastefulness of Beef Production" and "Diminishing Returns in the Fattening of Stock."

It will be good to turn from these questions of meat, upon which the Food Controller has already come to indisputably sound and saving decisions, the wicked nonsense uttered by the farmers at last week's conference notwithstanding, and to learn from Sir William's new pages how to feed the plant which is the staff of life and upon the supply of which our cause depends. And if I am allowed to return to the subject when the book appears, only the reader who does not eat will require an apology for my importunacy.

LENS.

THE IMPORTANCE OF SCIENTIFIC TRAINING.

SOME time ago, when Sir Arthur Newsholme (chief medical officer of the Local Government Board), was distributing the medals and certificates to the students of Keighley Grammar School, which, by the way, claims him as an "old boy," he took the occasion of emphasising in the course of his Address the importance of a scientific training in early educational life. It is a trite criticism that technical and scientific education in this country has not been accorded the fostering care and attention which it merits, and that the older system embracing a prolonged study of the humanities has been allowed to overshadow the more practical modern side. Be that as it may, Sir Arthur Newsholme struck at the root of the educational problem by declaring that the best service—in the home, in the community, and in the national life—would be that rendered by the best trained boys. The first and foremost essential in this training is that of character. Scientific training was of the highest importance—possibly there had been too little of it in the past—and though technical education was very necessary, it needed, as a motive force behind it, a sound grasp of the underlying scientific principles. It was only by attention to pure science as well as to applied science that they could hope to make advances and break new ground. The so-called "practical man" was not an ideal to be universally admired. He had his place certainly, but he generally worked by rule of thumb—that is, he did things as they had been done before. Now, it was not only necessary that a well trained lad should know what had already been discovered, but he should also be acquainted with the *methods* of discovery in order to take up his part in advancing the welfare of the community; in other words, what was really wanted was a knowledge of the principles underlying the practical action which they took. Turning to the broader aspect of the question Sir Arthur premised that there should be provision for research in all scientific teaching; that alone would provide an outlet for inventive faculty, and they would then be able to look for development and extension of their present knowledge and not be confined merely to teaching knowledge already gained. By a few apt illustrations from the works of Faraday, Röntgen, Prof. Maxwell, Sir William Crookes, and others he showed how, by proceeding along lines of correct theoretical reasoning, practical discoveries of immense importance had been arrived at, and of these wireless telegraphy, radiography, and numerous other achievements were a lasting memorial. Had these results been aimed at from the opposite direction, as, for instance, by a conference of surgeons sitting down to discuss how a foreign object such as a bullet embedded in the human body could be accurately localised or rendered visible *in situ*, the idea would have been laughed at as a practical impossibility. He further threw out the suggestion that some of the magnates of the district might see their way to encourage and subsidise research work on the industrial problems of the district, and no doubt it was gratifying to learn, through the seconder of the vote of thanks to Sir Arthur Newsholme, that something like £1100 a year for five years had just been granted towards establishing a county scheme for scientific research in connection with the textile industry.—*The Medical Official Journal.*

NOTICES OF BOOKS.

Science and Industry. The Place of Cambridge in any Scheme for their Combination. By Sir RICHARD T. GLAZEBROOK, C.B., M.A., F.R.S. Cambridge: At the University Press. 1917. Pp. 51. Price 1s. 6d. net.

THERE is much food for reflection in this little book, which contains the Rede Lecture for 1917, and it is to be hoped that it will be widely circulated among the educated public. The truths it contains are expressed both temperately and forcibly, and the author possesses a peculiar faculty for arresting the attention and putting his points clearly before his readers. In the first pages it is shown how modern warfare depends upon scientific investigation, while the debts which medicine and agriculture owe to science are equally great. An attempt is then made to clear up the confusion of thought by which modern civilisation is called materialistic because it deals with matter. It is pointed out that civilisation is rather to be described as the creation of the human spirit, the outcome of the slowly-won triumph of the spiritual in bringing matter into subjection. This is a truth which undoubtedly needs emphasising, for many, both among men of science and the unlettered, have failed to achieve clear thinking on the subject. The lecturer then proceeded to show how there are necessarily three different stages in the successful union of science and industry. Discoveries must first be made by the men who are specially endowed with love of knowledge and a gift for research, those whose one desire is "to discover the truth and apply the consequences fearlessly"; the technical applications of these discoveries must be studied in laboratories of industrial research, where new processes and products are examined and developed, and finally the works where the finished product is turned out must be provided with its own controlling works laboratory. In conclusion, the lecturer touched upon a very important point, namely, the need for the formulation of a scheme of general scientific education suitable for all boys and girls who are not necessarily going to specialise in science. It is clearly the business of teachers of science to work this out, and it is a task the utmost importance to the welfare of the nation, for the place of compulsory Greek will have to be very carefully filled if we are not to run the risk of substituting King Stork for King Log.

Practical Chemistry for Medical Students. By ALEXANDER CHARLES CUMMING, D.Sc. Second Edition. Edinburgh: James Thin. 1917. Pp. 165.

THIS course of practical work in chemistry is designed especially for medical students, but might also be found suitable for general purposes. The work described requires only simple apparatus, and all the experiments are easy to perform. A good preliminary course of work on the properties of common substances, the preparation of gases, salts, &c., is given, followed by a short section on volumetric analysis and a full course of qualitative analysis for the more common elements. Special attention is called to pharmacopœial preparations, and some organic substances are included. In the new edition experiments on bread, fats, potatoes, &c., have been added, and some minor changes have been made, but the general plan of the book remains unaltered.

Introduction to the Rarer Elements. By PHILIP E. BROWNING, Ph.D. Fourth Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1917. Pp. x+250. Price 7s. net.

THIS valuable work has for some years been regarded as quite indispensable to students who are taking up the study of the rarer elements, and for those who wish to undertake research work on the subject. It was originally prepared from material used by the author in a short lecture course given at Yale University. Brief accounts are given of the history and properties of the rarer elements, with references to original literature and to longer works for fuller details, and about 200 experiments are described illustrating methods of preparation and separation and the formation of the most important derivatives of the elements. In the fourth edition the chapter on the radio-elements has been thoroughly revised by Prof. B. B. Boltwood, who wrote it for the second edition, and the sections on gallium, indium, and germanium have been much extended. The chapter on the technical applications of the rarer elements contains a good deal of fresh material, and a new plate shows the spectrum of gallium and the arc spectra of some gallium and indium products.

Refining and Utilisation of Georgia Kaolins. By Ira E. Sproat. Washington: Government Printing Office. 1916. Pp. 59. Price 15 cents.

This bulletin describes the work which has been done in investigating the refining of American kaolin, in order that it may be used in place of that imported from England. Large quantities of kaolin are found in Georgia and South Carolina, but owing to the fact that it possesses an abnormal shrinkage it has not hitherto found application for the manufacture of tile and white ware. By a new process of purification a material has now been obtained which can be used as a substitute for all the ball clay and 50 per cent of the English china clay imported. The method depends upon the fact that the addition of alkalis to clay and water systems increases the dispersion. Carefully controlled quantities of caustic soda are added to clay and water in a washer, and the heavy minerals present are thus precipitated, while the clay remains in suspension. The caustic soda is subsequently neutralised with sulphuric acid and the clay is filtered off. The success of the process depends upon the technical control of the viscosity, and indeed, of every step in the process, but the cost is comparatively low, and the product appears satisfactory in every respect.

CORRESPONDENCE.

BLINDED SOLDIERS' CHILDREN.

To the Editor of the Chemical News.

Sir,—I want to carry one step further the endeavour which during nearly three years past has been made to brighten and render useful the lives of the soldiers and sailors who have been blinded in the war.

The success of the work at St. Dunstan's has exceeded my most sanguine hopes, and the system of after-care which has been organised is carrying on that work with complete satisfaction.

Now I feel that everything possible should be done to encourage the bachelor blinded soldiers to marry and surround themselves with children, and also to help those already married with the new babies who may come to them. I am thinking not only of the joy thus to be brought into their lives, but of the practical help of a wife and children to a man who is sightless.

And the Empire will want the sons and daughters of men like these.

The Government make a weekly allowance for children born before or within nine months of the soldier's discharge; but there is, of course, no allowance for the children born later or for those of the men who marry after leaving the Army because of their disablement.

There is, it seems to me, something infinitely pathetic about the idea of these children whom their fathers will never see. They will be known only by the sound of their voices and by their characters as they develop. Their little faces will become familiar by the touch of the hand that caresses them. And they will grow up to responsibilities that other children do not know. It must often fall to the children of the blind man to be the special companion of their father, to wait on him, to guide him, to become, in a sense, the guardians of their parent.

I feel certain that those whose joy it is to look on the faces of their children, to watch their smiles and their play, to see them grow up, will be eager to help the men from St. Dunstan's to care for the little ones, known to them so strangely, like the children we see in our dreams.

The heroism of the blinded soldier is not a matter of the battlefield alone, for to face life joyously and usefully in a world that is dark requires an enduring courage. The generous help that has come to me for these men seems to be a message from the public that they want them to live the happiest lives possible; we do not want the men who have given their sight for us to be hampered by difficulties that forethought can remove from their way. To give blind soldiers the assurance that the children who come to brighten their lives shall be provided for till they are able to make their own way in the world is the object I have at heart.

It is wonderful for the blinded soldier to have the love and constant care of a wife. And in a world of darkness what visions of light are called into existence by the laughter of children, the sound of their feet, the touch of their hands?

It is my hope to be able to raise a Fund to provide an allowance of 5s. per week until the age of 16 for each of these children who are not cared for by the State.

The total required will certainly amount to—and may even exceed—£250,000. A sum so large can only be raised by an effort worthy of this cause, which will, I am sure, appeal to everyone.

May I beg the hospitality of your columns to ask for the support of your readers both for subscriptions and for help in collecting this Fund?

The object is one which will, I am sure, appeal above all to the women of this country.

All requests for information and all donations should be sent to me at 224, Great Portland Street, London, W.1, and marked "Blinded Soldiers' Children Fund."—I am, &c.,

Arthur Pearson.

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THE CHEMICAL NEWS

Vol. CXVI., No. 3018.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

Part I.—Solids.

By IRVING LANGMUIR.

(Continued from p. 145).

The action of oxygen in preventing the dissociation of hydrogen by a heated tungsten filament is clearly that of a *catalytic poison*. It has been shown previously that the dissociation of hydrogen takes place only among hydrogen molecules adsorbed on the surface of the tungsten (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 1145). The only way in which oxygen can prevent such action in a high vacuum is by the actual presence of oxygen atoms on the surface. Since the dissociation at 1500° K. is entirely prevented by the oxygen, and since the range of atomic and molecular forces does not exceed the dimensions of the atoms, it must follow that much more than half the surface must be covered by oxygen atoms or molecules. For if the surface were only half covered then, according to probability laws, uncovered areas several times as large as the diameters of atoms would not be of rare occurrence, and on these areas dissociation could occur.

Now, if this adsorbed oxygen were present on the surface as a layer of compressed gas it would be inconceivable that it should not react at all with hydrogen at a temperature of 1500° K. (The commonly accepted theories of adsorption are based upon the assumption that there is a transition layer—van der Waals—in which the density varies gradually from that of the solid or liquid phase to that of the surrounding gas. Eucken—*Verh. Deut. Physik. Ges.*, 1914, xvi., 345—for example, considers that this transition layer is a sort of miniature atmosphere. Bakker—*Zeit. Phys. Chem.*, 1915, lxxxix., 1—has a similar theory to account for surface tension phenomena). Even if we should regard the adsorbed layer as consisting of adsorbed tungsten oxide we would be no nearer an explanation, for tungsten oxide is readily reduced to metallic tungsten by hydrogen at temperatures of 500°. We should have to say, with Bancroft, that the oxide is stabilised by adsorption. But, of course, this is a mere description and not an explanation of the phenomena.

It is very clear that the oxygen by being adsorbed has undergone a complete change in chemical properties, and it is certainly not logical to consider that this has been brought about by a mere compression of the gas into a surface layer.

If, however, we assume that the oxygen atoms are chemically combined to the mass of the tungsten filament and form a *continuous* surface layer all of the observed facts are readily accounted for. The oxygen atoms are saturated chemically by the tungsten (primary valence), and the field of force holding the oxygen atoms lies wholly below the surface where hydrogen molecules cannot reach it. When the pressure of oxygen falls so low that the supply of this gas at the surface is not sufficient to make up for the loss by evaporation then gaps are formed in the continuous covering, and the hydrogen is then able to make a *flank attack* on the oxygen. In this way the oxygen covering is *suddenly* removed when the pressure of oxygen falls below a certain critical value, and the dissociation of hydrogen therefore begins at once. (The strongest evidence of the correctness of this theory is obtained from experiments at higher filament temperatures than 1700° K. The hydrogen and oxygen then begin to react with each other on the surface of the filament. The further development of this theory is reserved for a future paper in which the detailed experimental results will be published).

The resemblance between the action of oxygen on a tungsten filament and the phenomena of electro-chemical passivity is very striking, so much so, in fact, that the mechanism of passivity is probably similar to that of the effects described above. (An outline of this theory of passivity together with a brief description of the experiments with mixtures of oxygen and hydrogen in contact with a hot tungsten filament was given by the writer in a discussion of Bennett and Burnham's paper on "Passivity," at the Washington Meeting of the American Electrochemical Society, April 28, 1916. This discussion has been published in vol. xxix. of the *Transactions*).

According to this theory the effect of oxygen in poisoning the catalytic activity of tungsten is due to the formation of an exceptionally stable film of oxygen which is combined with and completely covers the surface of the tungsten.

The effects of the poisoning of tungsten by oxygen are also to be seen in many other reactions in gases at low pressures (10—100 bars), of which the following may be briefly mentioned.

When a tungsten filament is heated in a mixture of carbon monoxide and oxygen, tungsten is oxidised just as if no carbon monoxide were present. None of the CO reacts with the oxygen even when the filament is heated as high as 2800° K., whereas hydrogen begins to react with oxygen in contact with a tungsten filament when the temperature exceeds about 1700 K. Evidently CO will not combine with oxygen adsorbed on a heated tungsten filament even if it has a chance to make a "flank attack."

Mixtures of methane and oxygen at low pressures do not react with one another in contact with tungsten at 1500° K., or even 1800° K., but the tungsten is oxidised to form WO_3 as in the previous cases. In absence of oxygen methane is gradually decomposed, setting free hydrogen, while the carbon is taken up by the tungsten filament, forming a solid solution. Even this action is prevented by the presence of traces of oxygen. On the other hand, if the filament is first heated in methane so that it has taken up carbon, and then oxygen is admitted, the oxygen reacts with the carbon in the filament forming CO, and until all the carbon from the surface layers has been removed, the oxygen does not react with the tungsten. This proves that when carbon is taken up by tungsten some of the carbon remains as an adsorbed layer of carbon atoms.

Dry ammonia at low pressures is decomposed fairly rapidly by a tungsten filament at 1000° K., but with a platinum filament the same rate of decomposition only occurs at a temperature of nearly 1400° K. In the presence of small amounts of oxygen, however, the tungsten filament fails to decompose ammonia even at 1200° K. At 1300° K. the tungsten oxidises just as if the ammonia were absent, the oxide WO_3 distilling to the bulb. Some of the ammonia seems to react with the oxygen, but with an excess of ammonia this reaction goes on slowly until the oxygen is consumed, and the remainder of the ammonia is then rapidly dissociated. The oxygen thus poisons the tungsten even in the case of the simple dissociation of ammonia by heat. In contact with platinum, however, ammonia and oxygen react together at a temperature well below 1000° K. Particularly interesting effects are observed when a tungsten or platinum filament is heated in mixtures of cyanogen and oxygen. In this case, with a filament at 1500° K. the oxidation of the tungsten is largely prevented until the cyanogen has been slowly oxidised to carbon monoxide and nitrogen. If there is an excess of oxygen this then reacts with the tungsten when the supply of cyanogen is used up. Any excess of cyanogen is decomposed by the filament giving nitrogen, the carbon being taken up by the filament. Thus cyanogen may be looked upon as having a stronger poisoning effect on tungsten than oxygen has.

It is well known that cyanogen poisons the catalytic activity of platinum. Experiments at low pressures furnish a remarkable demonstration of this fact.

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* From the *Journal of the American Chemical Society*, xxxviii., No. 11.

A platinum filament at a temperature of 600° K. causes carbon monoxide and oxygen to combine rapidly, the carbon monoxide, however, itself acting as a catalytic poison (Langmuir, *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1163). At higher temperatures (900° K.) the poisoning effect of the carbon monoxide disappears, and the velocity of the reaction becomes enormously high, being then limited only by the rate at which the two gases can come into contact with the platinum surface, according to Equation 4.

But if a trace of cyanogen is added to the mixture of oxygen and carbon monoxide (at a pressure of 10 bars) the catalytic action of the platinum disappears completely even at 900° K. By raising the temperature to about 1000° the cyanogen reacts with the oxygen to form nitrogen and carbon monoxide. As soon as the cyanogen is all oxidised the catalytic activity of the platinum is restored, and the oxygen and carbon monoxide then react rapidly to form carbon dioxide.

The catalytic effect of platinum on the reaction between oxygen and hydrogen is also poisoned by traces of cyanogen. If the temperature of the platinum is then raised the cyanogen and hydrogen react together to form hydrocyanic acid.

The fact that these low pressures of cyanogen (or oxygen) can exert such a powerful poisoning effect is proof that adsorbed films of great stability are formed; in other words, films in which the rate of evaporation of the adsorbed molecules is remarkably low. The effect of these poisons is thus merely to cover up the active surface.

The property of cyanogen in poisoning metallic catalysers is thus closely related to the chemical facts that cyanogen forms very stable compounds with metals, and shows an unusual tendency to form complex salts. The cyanogen radical is one in which both the primary and the secondary valencies are strongly developed.

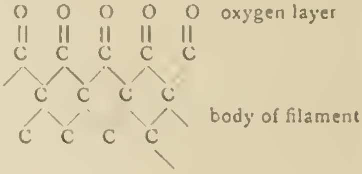
Water vapour has the same effect in poisoning the catalytic activity of tungsten that oxygen has. A partial pressure of 0·4 bar of water-vapour (vapour pressure of water at −78°) is sufficient to prevent the dissociation of hydrogen by a tungsten filament at 1500° K.

It is a remarkable fact that carbon dioxide, although it oxidises a tungsten filament to form WO_3, does not have any effect upon the rate of dissociation of hydrogen. We must therefore conclude in this case that only a very small fraction of the tungsten surface is covered by adsorbed oxygen. This conclusion is also supported by the fact that the rate of oxidation of tungsten by carbon dioxide is extremely slow compared to the rate of oxidation by oxygen. We shall see that further evidence of the same kind is furnished by measurements of the electron emission. However, since the oxygen from at least two molecules of carbon dioxide is needed to produce a molecule of WO_3, it is certain that the reaction depends upon the presence of adsorbed oxygen partially covering the surface. The velocity of the reaction between carbon dioxide and tungsten seems to be approximately proportional to the square root of the pressure of CO_2 and inversely proportional to the pressure of carbon monoxide.

When molybdenum filaments are heated in oxygen at low pressures the filaments become tarnished unless the temperature is maintained above 1500° K. Above this temperature the surface of the filament remains apparently clean, and the oxide formed, MoO_3, distils to the bulb. With tungsten, notwithstanding the fact that WO_3 is much less volatile than MoO_3, it is only necessary to keep the temperature above about 1250° in order to have a clean surface.

Although oxygen is clearly adsorbed on molybdenum it appears that the stability of the film is much less than that f the corresponding film on tungsten. This is shown not nly by the electron emission (see below), but by the mparatively small effect of oxygen in poisoning the catalytic activity of molybdenum. Thus when molybdenum is heated to a temperature between 1500 and 1800° K. in a mixture of oxygen and hydrogen, it is found that the hydrogen disappears slowly until the oxygen is all used up by reacting with the molybdenum. After that the rate of disappearance of the hydrogen is much greater. The fact that a part of the hydrogen disappears before the oxygen is consumed indicates that the poisoning effect of the oxygen is not complete.

Experiments with carbon filaments in oxygen, and in carbon monoxide or dioxide (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1154), have shown that oxygen acts as a catalytic poison on the reaction between oxygen and carbon, and on that between carbon dioxide and carbon. It was also proved that this poisoning effect is due to a remarkably stable film of adsorbed oxygen, so stable in fact that the filament must be heated in a good vacuum for nearly half-an-hour at 2300° K. in order to distil it off. In this case there is very clear evidence that this film consists of oxygen atoms chemically combined by primary valencies to the carbon atoms forming the body of the filament according to the formula—



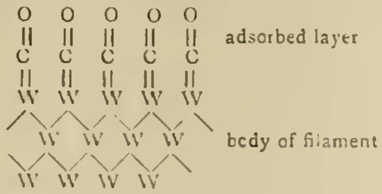
A very peculiar case of adsorption occurs when a tungsten filament is heated to about 2700° K. in a low pressure of carbon monoxide contained in a bulb cooled by liquid air. (A brief preliminary account of these experiments was published in the *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1106. A more detailed paper will be presented later).

With the bulb at this temperature the tungsten filament is attacked by the CO, and a very stable adsorbed film is formed on the filament. This distils off at a constant rate (independent of the pressure of CO) taking the tungsten with it as a compound of the composition WCO. The most remarkable fact is that when the temperature of the bulb is raised to 20° or above, the CO no longer attacks the tungsten of the filament, but combines only with the tungsten which evaporates from the filament still forming the compound WCO.

Before attempting to look for the probable mechanism of this action let us consider one more case of adsorption; that of nitrogen by *molybdenum vapour*. When a molybdenum filament is heated to 2200° K. in nitrogen contained in a bulb cooled in liquid air, nearly every molybdenum atom evaporating from the filament combines with the *first* nitrogen molecule which it strikes to form a compound MoN_2 (stable at 360° in a vacuum). When the bulb is at room temperature the molybdenum atoms still combine with the first nitrogen molecule they strike, but most of the molecules thus formed are so unstable that they decompose when they strike the bulb, giving nitrogen and a spongy molybdenum deposit.

Thus when the nitrogen is at low temperature the compound appears to be MoN_2 in which the atoms are held by primary valence, while the compound formed with the nitrogen at higher temperatures is $Mo : N_2$, in which the nitrogen and molybdenum are held by secondary valence. This seems then to be a kind of adsorption of one gas by another.

A somewhat similar explanation seems necessary for the reaction between tungsten and carbon monoxide. Thus when carbon monoxide molecules of low velocity and low internal energy (low temperature) strike the surface of the filament they combine with it by primary valencies to form a stable structure, probably as follows:—



The strength of the union between the oxygen and carbon, and between the tungsten and carbon, is so great that the whole group WCO distils off as a single molecule. The fact that the tungsten is partially saturated by the carbon should make this group somewhat more volatile than the tungsten itself. As a matter of fact, the rate of evaporation of the WCO from the surface is only about five times greater than that of tungsten.

When the temperature of the bulb is higher so that the CO molecules possess more internal energy (and a higher velocity) the CO is incapable of combining with the solid tungsten in the above manner. We must still assume that nearly every CO molecule which strikes the filament condenses on it, but that the union in this case is by secondary valence, so that the molecule almost immediately distils off again.

A more thorough study of this reaction may throw some light on the paradox that the residual valence of CO is small, although this substance contains a divalent carbon atom.

The Effect of Gases on the Electron Emission from Heated Metals as Evidence of the presence of Stable Adsorbed Films.

The effect of adsorbed films of the thickness of a single molecule on the electron emission from heated tungsten filaments was described by the writer in 1913 (*Phys. Rev.*, 1913, ii., 450). A little later (*Phys. Zeit.*, 1914, xv., 520) the following theory of the effect was proposed :—" The decrease in the electron emission from a hot cathode caused by certain gases is due to the formation of a film on the surface of the cathode. Whether this film consists of adsorbed gas, or of a chemical compound of the gas with the cathode material, is not definitely established, but most of the evidence is in favour of the latter view. The amount by which the electron emission is affected depends on the *extent* to which the surface is covered. The film should be looked upon as consisting of a single layer of molecules, or at most of a very few layers. The extent to which the surface of the cathode is covered by the film depends upon (1) the rate of formation of the film ; (2) the rate of destruction of the film," &c.

The more recent work on chemical reactions at low pressures and further experiments on electron emission have furnished abundant evidence of the correctness of the above viewpoint, and have fully verified the conclusion that the film is held to the surface by chemical forces.

In every case with tungsten chemically inert gases have been found to be without effect on the electron emission, whereas nearly all gases that react with the tungsten lower the emission.

The decrease of the electron current produced by a gas is thus caused by the formation of an adsorbed film of great stability, which covers the surface. The evidence is very strong that the electron emission at a given temperature depends only on the nature of the layer of atoms forming the actual surface of the filament. Here, again, we have proof of the absence of a transition layer in which the density varies gradually from that of the filament to that of the surrounding space.

The lowering of the electron emission of heated filaments by adsorbed films thus bears a close relationship to the effect of these films in poisoning the catalytic activity of the filament. Both effects are caused by a film of great stability which covers the surface. The following experimental evidence shows, in fact, that there is a remarkable parallelism between the electron emission and the catalytic activity of a filament.

As has already been pointed out, oxygen enormously lowers the electron emission from tungsten. This effect of oxygen is in accord with its action as a catalytic poison for tungsten. Thus in mixtures of oxygen and hydrogen the electron emission undergoes a sudden increase at the moment at which the hydrogen begins to dissociate (after the consumption of all the oxygen).

It might be thought that the electron emission itself would have an effect on the chemical reactions occurring on the surface of a heated filament. But experiment has never shown any such direct effect. Thus the rate at which oxygen, hydrogen, carbon dioxide, and other gases disappear in contact with heated tungsten are found to be entirely independent of the thermionic currents. The presence of a negatively charged electrode close to the heated filament causes all electrons emitted to be driven back into the filament, but this does not affect the rate of disappearance of the gases. In some cases, however, electron discharges do cause the clean-up of gases, but this effect is due to the bombardment of the filament by positive ions and not to the electron emission.

Nitrogen does not normally attack a tungsten filament at any temperature, although it combines (to form WN_2) with tungsten vapour as fast as this evaporates from the filament (*Jour. Am. Chem. Soc.*, 1913, xxxv., 931). Similarly nitrogen has no effect on the electron emission from tungsten if low voltages are used in making the measurements of the thermionic current. But if voltages high enough to cause ionisation of the nitrogen are employed, then the tungsten is attacked by the rapidly moving positive nitrogen ions, and simultaneously the electron emission is greatly decreased, indicating that a film of adsorbed nitrogen is formed. If the filament is now allowed to cool to room temperature and the remaining nitrogen is pumped out, and the filament is then heated again to the same temperature as before, it is found that the electron emission is at first the same as it was in the presence of the nitrogen, showing that the electron emission is determined not by the gas around the filament but by the film adsorbed on it. Gradually the adsorbed film distils off, and the electron emission returns to its normal value.

By the study of such lag effects, the rate of evaporation and the rate of formation of the adsorbed films can be measured with accuracy, and it has thus been proved that the fraction of the surface covered often depends upon a dynamic equilibrium.

The fact that the rate of evaporation of these films eve at temperatures of 1800° K. is slow enough to measure proves that they are remarkably stable.

Extremely interesting phenomena are observed after a tungsten filament has been heated in CH_4 or C_2N_2, or other gas which give up carbon to the filament. The most minute trace of carbon (probably just enough to form a layer one atom deep over the surface of the filament is sufficient) in the surface of the filament cuts down the electron emission to about one-third of that of an uncontaminated filament. But a filament which has taken up carbon is no longer sensitive to the effect of bombardment by positive nitrogen ions. In other words, nitrogen has no effect on the electron emission from such a filament even if high anode voltages are used. Still more remarkable is the fact that oxygen instead of lowering the electron emission of a carbon-containing filament gradually raises it. The carbon is then gradually oxidised and the electron emission returns to the value corresponding to pure tungsten. Then when the carbon has all been removed, the oxygen begins to attack the tungsten, and the electron emission suddenly decreases to one per cent or less of its former value. After the excess oxygen has been consumed it is found that the electron emission is again sensitive to the effect of bombardment by positive nitrogen ions, the thermionic current decreasing as the voltage is raised.

This experiment is an excellent demonstration of the closeness of the relationship between the electron emission and the chemical activity of the filament.

Another illustration is afforded by the fact that water-vapour, which reacts rapidly with tungsten, and poisons the tungsten surface, has as great an effect on the electron emission as oxygen, while carbon dioxide, which reacts slowly with tungsten, and is not a catalytic poison, has practically no effect on the electron emission.

So far we have considered the effects of gases on the electron emission from tungsten. Striking effects of another kind are obtained when the filament contains minute amounts of thorium. (An account of these phenomena was given before the American Phys. Society, October 31, 1914—*Phys. Rev.*, 1914, iv., 544. A paragraph describing the effect was given in a paper before the American Electrochemical Soc.—see *Trans. Am. Electrochem. Soc.*, 1916, xxix., 353). If such a filament is heated in a very high vacuum to 2900° K. for a short time and the electron emission at 1800° K. is then measured, it is found that the emission is the same as that of pure tungsten. By now heating the filament a few minutes at a temperature between 2000° and 2500° K. (preferably 2300° K.), the electron emission at 1800° K. is found to have increased enormously (more than 10,000 fold). By heating again to 2900° the emission returns to its normal value.

This effect is due to the formation of an adsorbed layer of thorium atoms on the surface of the filament. At 2900° K. the thorium, being more volatile than tungsten, distils off the surface and leaves pure tungsten. At 2300° K., however, the rate of distillation is not very marked, but the rate of diffusion of the thorium through the tungsten is sufficient to allow the accumulation of thorium atoms on the surface. At 1800° the rate of diffusion is negligible, so that if the thorium is distilled off a fresh supply does not diffuse to the surface.

The tendency of thorium to form an adsorbed film on tungsten is in accord with other properties of thorium. Gibbs has shown that any substance which lowers the surface energy tends to be adsorbed on the surface. The Eötvös-Ramsay-Shields relation indicates that the surface energy of a substance at temperatures low compared to its critical temperature should be approximately proportional to $T_c A^{-2/3}$ where T_c is the critical temperature and A is the atomic volume. Now the critical temperature of thorium must be lower than that of tungsten, since the vapour-pressure of thorium is considerably greater than that of tungsten. The atomic volume of thorium is about 21, while that of tungsten is 9·6. Thus both T_c and A differ, for these metals, in such a way as to make the surface energy of thorium less than that of tungsten. Therefore, according to Gibbs' rule, thorium should tend to be adsorbed on the surface of tungsten.

By a study of the rate of growth of the adsorbed film at 2100° K. and the rate of evaporation at 2700° K. it has been possible to prove that the film grows until it is one atom deep, but does not grow beyond this. (That the layer is never more than one atom deep is readily proved by the fact that the activity of the film always begins to decrease *at once* at 2700° no matter how long it may have been previously heated at 2300° K.). The real evidence in favour of these conclusions, however, can only be given in connection with a full discussion of the detailed experimental results. It is intended to publish these before long.

When oxygen is brought into contact with a tungsten filament (at 1900° K.) coated with a layer of thorium atoms, the electron emission is suddenly decreased to a value far below that corresponding to pure tungsten. With tungsten the effect of oxygen in decreasing the emission disappears as soon as all the oxygen has been consumed. But with a thorium-coated filament the effect of oxygen is more permanent, so that the emission remains low even after all oxygen has been removed. Only by heating the filament to 2900° and following this by a treatment at 2300° can the activity be restored. This behaviour is in accord with the known facts that thorium has an unusually strong affinity for oxygen.

In the case of this oxidised thorium coated filament the adsorbed film evidently consists of a layer of thorium atoms covered by a layer of oxygen atoms. It should not be looked upon as a layer of adsorbed thorium oxide.

Interesting effects are observed if a small amount of methane is brought into contact with an oxidised thorium-coated tungsten filament at about 1900° K. The electron emission suddenly increases to that of pure thorium, and then as suddenly decreases to a value below that of pure tungsten. The methane reacts with the oxygen on the surface of the filament, forming carbon monoxide, which evaporates off, leaving the layer of thorium atoms. The excess of methane is then decomposed, and a layer of carbon atoms is formed on the surface of the filament, and covers the thorium atoms. The electron emission then becomes that of a carbon surface, which is a little less than that of tungsten, notwithstanding the presence of thorium atoms just under the surface layer.

Kruger and Taege (*Z. Electrochem.*, 1915, xxi., 562) have recently studied the effect of catalytic poisons on the photoelectric activity of platinum, using ultraviolet light. They find that minute traces of H_2S, HCN, or CO very greatly decrease the photoelectric electron emission. The mechanism of this reaction is undoubtedly identical with that of the effect on the thermionic electron emission. Debye (*Ann. Phys.*, 1910, xxxiii., 441) and Richardson (*Phil. Mag.*, 1912, xxiii., 266, 615; 1912, xxiv., 570) have shown that there is a very close relationship between the photoelectric and thermionic electron emission. (For a review of the recent work on this subject and its relation to contact potentials see a paper by Langmuir, *Trans. Am. Electrochem. Soc.*, 1916, xxix., 341).

(To be continued).

GLASS.*

The appearance of a new scientific journal is an event which, in ordinary times, might be allowed to pass without heed on the part of the general public. Specialist scientific journals appeal only to a certain and often not large section of the people, and they form no part of the general reading of even the highly educated and intellectually well-endowed members of the community. Nor could one expect it to be otherwise. But there may be times—and the present appears to be one of them—when the publication of a new and specialist journal should enter into the cognisance at least of the general educated public, as giving a sign of vitality and development in certain directions of human activity. And it is as such that one may note the appearance in this country of the first part of a new journal, the official organ of the Society of Glass Technologists, a society founded, in a time of industrial stress, for the purpose of fostering and of developing on scientific lines an industry of national importance. It is sufficiently well known to all that this country had allowed itself to drift into a state of great dependence on foreign countries, and more especially on Germany, for its supplies of scientific and optical glass—glass for chemical ware, for thermometers, for incandescent gas lamps, for miners' safety lamps, for electric light bulbs, for X-ray tubes, for optical instruments, &c.—and the outbreak of war placed this country in a position of some difficulty owing to a shortage of the necessary kinds of glass. The seriousness of our position was quickly realised, and great efforts have been made, and made with a considerable measure of success, not only to overcome the difficulties of the present, but also to lay a firm foundation for the future development of the scientific and optical glass industry in this country. One speaks so familiarly of glass as if it were a material of perfectly definite composition and properties, like iron or copper, that very many people do not realise the very large number of different kinds of glass called for by our modern civilisation, or understand the special difficulties in the way of manufacturing some of the most important varieties of the material, especially what is known generally as optical glass. As an effort is now being made in this country to develop the glass-making industry along directions which were largely neglected in the past, and as considerable public funds have been assigned by the Research Committee of the Privy Council for the purpose of establishing this industry on a scientific basis, such as would render this country largely independent of foreign supplies of glass ware, it is desirable that the general public also should possess some knowledge of the industry, at least in its more general aspects.

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* From *The New Statesman*, September 15, 1917.

Glass is not a single substance, but a homogeneous mixture of substances known as silicates. If one heats quartz or silica, which occurs naturally in great abundance as sea-sand, with carbonate of soda or potash, the silica displaces the carbonic acid from the carbonate, and a fusible compound, sodium silicate or potassium silicate, is formed. On allowing this to cool, a glassy material is obtained, known familiarly as water-glass, by reason of its solubility in water. If, however, the quartz or sand is fused not only with soda or potash, but also with the oxides or carbonates of other metals like lime, alumina, red lead, &c., a molten mixture of silicates is produced which solidifies to a glassy mass which no longer dissolves in water and constitutes what is ordinarily known as glass. Although all glasses contain either soda or potash, the other basic constituents may be varied not only in kind but also in amount.

In the manufacture of glass the intimate mixture of the ingredients (sand, soda—or potash—white chalk, or carbonate of lime, &c.) is melted in large fire-clay pots, placed in fornaces which are now generally heated by gas. When first melted, the contents of the pot are permeated by innumerable bubbles of carbonic acid gas, which ender the mass almost opaque. In time, however, these bubbles escape and leave a clear liquid from which the desired articles can be formed either by pouring the glass into moulds or by means of a blowpipe.

Ordinary window glass, bottle glass, glass for tableware and for general use consists essentially of a mixture of the silicates of soda and lime, but small quantities of aluminium silicate are also frequently present. "Crystal" glass is essentially a mixture of potassium and lead silicates. Although the composition of the glass in ordinary use is subject to variation, the quality and appearance of the glass depend mainly on the purity of the materials used in its manufacture. Since the presence even of exceedingly minute traces of certain metals imparts a colour to the glass, great care must be taken, in the case of the best quality glass, to use pure materials. Since iron is the impurity most frequently met with, the glass obtained has frequently a more or less pronounced green colour, especially noticeable in the cheap bottle glass made from the less pure forms of sand. A slight green colour is also noticeable in practically all old window glass. Sometimes this green colour is "corrected" by the addition to the glass mixture of a small quantity of black oxide of manganese, the presence of which imparts an amethyst colour to the glass and so neutralises the green colour due to iron. The glass, therefore, appears white. When such glass is exposed for a lengthened period to bright sunlight the amethyst or purple colour due to the manganese becomes evident. Many examples of glass which has acquired this amethyst colour can be seen in the window-panes of older houses much exposed to the sun.

After the glass has been fashioned into its final form it must be "annealed" by being heated to near its softening point and then allowed to cool very slowly. The purpose of this is to get rid of the stresses which are set up in the rapidly-cooled glass, and which render it very liable to fall to pieces when scratched.

Until comparatively recent years the materials used in glass-making consisted only of silica, soda, potash, lime, and oxide of lead, and although the properties of the finished glass could be altered by varying the proportions of these materials, the possible variation of properties was restricted. For the construction of microscopes, telescopes, and other optical instruments, opticians could command only two types of glass—the so called "crown" glass (a soda-lime glass), and "flint" glass (a potash-lead glass); and although the optical properties of these glasses could be varied somewhat, it was first clearly recognised by Ernst Abbe, who took up the study of the subject, on the invitation of the firm of Carl Zeiss, of Jena, that no great improvement in optical apparatus could be looked for until the existing limitation of glass-making materials was broken down and a much greater variety of glass made available. In 1881 Abbe, in collaboration with Otto Schott, commenced a systematic investigation of the elements for the purpose of discovering which of them were suitable for use in the manufacture of glass and what was the effect of each on the properties of the product.

As a result of these investigations, and of later investigations carried out in the same spirit, the range of materials of value in the manufacture of glass has been greatly extended so as to include, besides those previously in use, boric acid and phosphoric acid, alumina, baryta, magnesia, zinc oxide, calcium fluoride, arsenic, and antimony. With the materials now available, the glass manufacturer is enabled to produce many scores of different glasses, possessing peculiar and valuable properties—resistance to the action of hot acids and alkalis, resistance to rapid changes of temperature, ready fusibility, difficult fusibility, &c.—the existence of which makes possible the construction of scientific and industrial apparatus by which knowledge and the material well-being of the peoples have been promoted. It was as a result of these scientific investigations that the glass-making industry, especially in Germany, ceased to be carried on by rule-of-thumb methods and became a highly scientific industry controlled by the chemist and physicist. Although we had, in this country, allowed ourselves to become almost entirely dependent on foreign sources for our supply of special scientific and industrial glass ware, it ought to be made known and gratefully recognised by the people of this country that almost immediately on the outbreak of war the Institute of Chemistry appointed a Glass Research Committee to assist in overcoming the great difficulties into which this country had fallen through the cutting off of those supplies. As a result of the labours of that Committee, a large number of formulas for different kinds of glass have been supplied to glass manufacturers, so that now this country is in a position of independence as regards many of the most important kinds of scientific and industrial glass. Owing to the extension of the range of materials employed, optical glasses exhibiting great variation of refractive and dispersive power and of what is called the v-value (ratio of refractive to dispersive power) have also been produced. Great advances have in consequence been made in the design and quality of microscopes, photographic lenses, and other optical apparatus.

The production of optical glass, which has also been the subject of investigation by the Committee of the Institute of Chemistry, as well as by members of the staff of the National Physical Laboratory, encounters certain difficulties and necessitates methods of manipulation not met with in the case of other kinds of glass. Not only must the materials employed be of a high degree of purity so as to ensure a glass of great transparency, but the glass must also be as free as possible from gas or air bubbles and from solid particles produced by the partial crystallisation of the ingredients. Moreover, owing to the fact that glass consists of different ingredients which, on melting, do not at once form a homogeneous mixture, striæ or streaks of liquid of different refractive powers are produced. As the presence of these in the finished glass would be fatal for optical purposes, they must be got rid of by slowly stirring the molten mixture in the pot, a method first introduced towards the end of the eighteenth century by the Swiss watchmaker, Pierre Louis Guinand

At the conclusion of the process the glass is not removed as in the making of ordinary glass ware, but is allowed to cool down in the pot, during which process the latter breaks. As the making of a pot is a long and laborious operation which may extend over nearly a year, and may, even then, end in failure, and as only about a quarter of the glass melted is found to be usable, it will readily be understood that the cost of manufacture of optical glass is very considerable and will require extreme care and scientific control if it is to be remunerative.

Formerly British glass makers depended almost entirely on foreign sands, more especially the pure white sand from Fontainebleau, for the best kinds of glass; but it is clear that if this country is to succeed in developing the manufacture of chemical and optical glass as a national industry, it must be able to draw on a home supply of this most important glass constituent. The investigation of British resources of high-grade glass-making sand was, therefore, a matter of urgency and importance; and the results of such an investigation carried out by Professor P. G. H. Boswell ("A Memoir on British Resources of Sands Suitable for Glass-making," Longmans) have recently been published. From this Report it is satisfactory to learn that, so far as the existence of suitable sands is concerned, this country can be entirely self-supporting, even in the matter of optical glass. There are, indeed, no real and inherent reasons why this country should not make up the leeway of the past and why she should not excel in the glass-making industry. But if she is to do so, industry must join hands with science, and extensive and persistent research must be combined with business enterprise and manufacturing skill. A propitious start has been made; let there be no going back.

ALEX. FINDLAY.

THE GOLDEN APPLE.

SECRETS OF HEALTH AND FRUITFULNESS.

By SAMPSON MORGAN.

OVER thirty years ago I orginated the Fruit Growing Movement, which proved a remarkable success and gave a great impetus to commercial fruit culture on advanced lines.

One of its main principles was the substitution of the dwarf for the standard tree. Simultaneously I initiated the Fruitarian Movement, proving the perfect suitability of perfect fruit for perfect food, in the columns of the London *Echo*.

Then to assure the provision of ample fruit I started a land law reform propaganda through the National Fruit Growers' League, which I founded, with excellent results, the late Mr. W. E. Gladstone commending my work in this connection. Finally, I introduced the new soil science of clean culture, based upon forty years experiments, by which I have, I insist, conclusively proved that farm manure and all waste animal matter corrupt the soil and interfere with fertility, rendering the production of fruit of perfect tissue impossible.

As the result of my persistent commendation of the apple, it has come right to the front, and has even become of more importance than the orange. Why do I term it golden? Because under proper conditions it puts gold into the pockets of millions of producers, shippers, and distributors, and enables the toiling millions in the cities especially to enjoy the golden prize of health.

In 1911 I was commissioned to select and purchase a quarter of a million fruit trees, bushes, and fruit tree stocks for a gentleman of title, now a well-known peer connected with the London press.

They were planted on clean culture lines, and the first year afterwards apples 14 inches in circumference were gathered from some of the trees.

For some years, as far as my very limited opportunities and resources would permit, I have persistently experimented with clean culture in various ways, so that if I write emphatically it is because I have ample grounds for doing so. I have grown record crops for four separate products particularly, and this year my experiments with little apple trees have surpassed all previous records, simply because they are older, being now four years planted from the nursery. My plot is quite small, over half an acre. All the work connected with it I do myself, without any outside help at all, and in my spare time. Under these conditions the results obtained are of especial significance.

Much is due to my simple and natural method of pruning, but after all food is the dominating factor, for in every sphere of activity, seen and unseen, the universal cry is: We are what our food makes us. Soils and trees are no exception to that rule. The oneness of the universe is undoubted. It is an organic whole.

It is astonishing what an interest most people take in the apple. The premier fruit planting peer previously referred to above, makes it a daily practice to eat one apple at least all the year through. When perfectly matured, and few on sale in the cities unfortunately are, it is the greatest dainty imaginable, ahd if clean culture grown, its sugary tissue is easily digested, melting like cream on the palate.

It is rich in wholesome acids, and its juice, pure distilled water of nature, is of priceless worth, acting as it does in the most effective manner upon the earthy accumulations in the system, which are the primal cause of old age and many premature deaths. The tissue and juice of the apple make for health and the prolongation of life, because they make for flexibility. The fresh apple has been found to contain 13·0 of carbohydrates and 8·46 of water; the latter is literally worth its weight in gold when from fruits perfectly matured. The dried apple contains 62·0 of carbohydrates, and in this state is richer in such than the much boomed banana. The food value of apples depend upon their sugar contents. It is possible to double this under clean culture ash fertilisation. One writer has shown that whilst some apples may contain 6·83 per cent, the English Golden Pippin contains 10·36. This famous old variety, which a century and more ago was very popular in London, has never been surpassed by any competitor as far as sugariness is concerned.

Is it possible to induce a young dwarf apple tree four years planted from the nursery to produce a bushel of fruit? That was the question I set myself to answer in 1917, and I have demonstrated that it can be done, although the feat has never been accomplished by anyone anywhere.

The fruits have been seen on the trees and counted. I inserted a notice in the *Western Morning News*, whilst the trees were in fruit, offering to have a photograph taken for anyone free upon payment to the photographer of his charge alone. The actual apples are now on show to the public in several leading cities.

I have experimented with apples for size, colour, flavour, sugariness, fertility, and keeping properties. With regard to size and general appearance the results this year have been most marked. I select a few trees and their crops for the purpose of justifying the claims of clean culture.

One of the trees bore 80 yellow skinned apples, most of which weighed 8 ounces. They were cooking apples. Another tree produced 90 handsome red smudged fruits, being literally smothered with glowing specimens, forming, what I do not hesitate to term, the most shapely, fruitful, and prettiest apple tree in the world. It turned up quite by accident. It is of continental origin, and I doubt if any expert in the United Kingdom could correctly name it. It caused me considerable trouble to do so.

These two prolific trees form striking object lessons. The former is of British origin. This British apple equalled the continental one in size of fruit and yield. But for prettiness the latter took the palm. I have not yet tested the cooking quality of the foreign sample for it is not yet mature, but I am sure it is perfection.

Though the English specimen is simply splendid I am perfectly satisfied, however, that if 5000 bushels of the foreign apples with their glowing red coats were put upon any large wholesale market in Britain they would sell at sight forthwith at good prices. Hardly one of the 90 apples vary in size, shape, or colour. The ash fertilisation of clean culture greatly enhanced their colour.

The following details relate to other trees taken haphazard. On one, on a surface space only of 18 inches by 7, are 22 good sized apples, beautifully coloured, growing apparently in one cluster. Several Cox's Orange Pippin trees have from 80 to 120 richly coloured fruits.

An early culinary variety 5 feet in height including this year's new growth had 250 apples; 150 were thinned out, and the 60 left on to perfectly mature—the other 40 had been used—are from 9 to 10 inches in circumference.

I have many apples measuring 14 or 15 inches in circumference, although the swelling period has yet six weeks to run. Many Bramley's Seedlings measure 12 inches in circumference. A tree on a surface space of 17 inches by 10 has 17 fine apples, showing an unbroken surface of warm coated King of the Pippins. It has 60 apples even within 32 inches of the ground.

A Peasgood's Nonsuch only 4 feet high, the only one I have, has 26 grand fruits, each from 12 to 13 inches round, weighing on an average 13 ounces each.

What do the records of the trees referred to which bore a bushel of apples each mean, if they mean anything at all? Simply this, that it is possible to obtain these fruits at the rate of 600 bushels an acre, although 75 bushels from such trees would be considered a bumper harvest when fed with manure, though seldom has even that yield been enjoyed.

An Essex fruit raiser claims to have grown 300 bushels of apples from an acre of single cordon trees. I do not doubt it. When this incident came to my mind as I was writing this article, I put my pen aside, and went out and up to the first single cordon apple tree I met. It was in full fruit from top to bottom, carrying 30 late apples, the total weight of which was 7 pounds. These also had six weeks to continue swelling. That is at the rate of 600 bushels of apples to the acre. Until I tested this tree, as the result of writing this article, I was not aware it would give such results. Now these astonishing totals are due to several things, one of which is that with thorough aeration and the provision of bland non-forcing plant food, such as broken-down turf or decayed tree leaves, or leaves of succulent vegetables, such as cauliflowers, or green manuring by ploughing in mustard and such like, together with fine dus of the primary rocks, such as granite, or failing granite dust and a slow acting form of lime, wood, or bonfire ash, we may assure the healthy soil—the foundation of all fertility. From the healthy soil we get the healthy plant and tree; from the healthy plant and tree, the healthy fruit and grain, and these in turn fed to cattle and men assure the elaboration of healthy disease resistant tissue in the animal organism. Here, then, we have the natural, and because natural true, secrets of health and fruitfulness in the vegetable and animal kingdoms. Without the healthy cell there can be no healthy organism. The cry of all things which live is: We are what our food makes us. In the face of this argument the transcendent importance of the new soil science of clean culture is undoubted.

Soil made up of cloddy lumps of hard clay and lacking humus is useless for fruit culture, although the chemist says that it is rich in plant food. Chemicals will not render it suitable for fruit-tree culture. Without humus it is practically useless. It is the humus which will ameliorate it and enable the cultivator to break down and fine the cloddy lumps, and facilitate the production of that fine tilth which is a vital factor in all productivity.

Humus is produced by the decay of animal or vegetable matter. It is the great nitrogenous principle in soils. In turf of parks or prairie pastures we have the most perfect form of plant food known, and it consists of mineralised humus, the last word that can be said in plant foods and fertilisation.

With it any and every crop can be raised in profusion. Its carbon, nitrogen, and ash constituent are so deftly blended together that I question if the wit of man is capable of equalling, much less of surpassing it, in all round effectiveness.

Dead animal material and animal waste matters degrade the earth by fouling it, and in time induce soil sourness which is detrimental to the nitrifying or good soil organisms; that is, organisms good from the point of view of the cultivator and consumer.

Soil fertility is best maintained by supplies of plant food in the form in which it is furnished in turf. The growers should place greater reliance upon labour than upon manure and unduly forcing artificials, which are of a disease engendering nature, if they wish to enjoy bounteous harvests of golden fruits and grains.

THE DAY OF THE CHEMIST.*

By FRANK S. WASHBURN,
President American Cyanamid Company.

"Si monumentum quaeris, circumspice!" (If you seek his monument look around you). As we look around us, we see hardly a single object that has not required in its preparation the service of a chemist. The tungsten lights illuminating this room are the product of many years of patient toil. The glassware on the table and the eye-glasses that many of you are wearing are representative of two thousand different grades of glass that can be produced by the skilled glass maker who works under chemical control.

The cutlery on the table represents several immense branches of chemical industry—the iron and the steel industry and the mining industries. The making of iron and steel is in its every step controlled by chemical analyses, and recently many forms of steel have been produced as a result of systematic chemical experimentation. The extraction of silver and gold from their ores by means of cyanide solutions, and their purification, are chemical operations of great importance.

The clothing we wear would be a far different commodity if it were not for the chemist. The dye industry is attracting a great deal of attention since the war cut us off from German sources of supply. The American chemist and American capital are making good headway in their efforts to place this country on a basis, which if it is not independent, will at least not be entirely at the mercy of foreign sources of supply.

Cotton, which supplies such a large portion of the clothing of mankind, has a host of other uses. Fabrikoid, an artificial leather, is produced by nitrating cotton in a particular way and applying it to cotton cloth. For many purposes it is superior to ordinary grades of leather, and is much cheaper. Celluloid and similar compounds are made from cotton and have the widest variety of applications. Photographic films familiar to all of us are also made from nitrated cotton.

Perhaps the largest use of nitrated cotton to-day is in explosives, and this product of the chemist's art is playing a considerable part in determining the future of Europe.

Then, coming to the food, even the butter may not be above suspicion of having been tampered with by the chemist, and it is not unlikely that a great part of what we have partaken to-night was grown with the aid of chemical plant foods. Nitrogen drawn from the air, from coal, from distant Chile, and from various seeds, phosphorus from phosphate rock, and potash separated by careful crystallisation from the mother ores in Germany, have all helped to sustain the life of the plant and made it grow abundantly and well. Over 100,000,000 dols. are invested in fertiliser manufacturing plants in this industry, and for its products the farmers of this country pay 175,000,000 dols. per annum.

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* Address delivered at the Banquet of the American Chemical Society, Waldorf-Astoria Hotel, September 29, 1916.

The scientific preparation of new food products, the principles underlying the canning of fruits, all require the chemist. The preservation of foods by artificial refrigeration is made possible with ammonia produced from the air or in the coke ovens.

Cottonseed oil, in its raw state unfit for human consumption, is purified by chemical means and becomes a substitute for olive oil, or it is treated with hydrogen in the presence of a nickel catalyser and becomes a semi-solid.

Fruit oils, flavouring extracts, perfumes are made to-day synthetically, in a great variety and of high purity—some of these products surpassing the natural substances.

And when you ride home in your automobile to-night the motive force in the engine will be gasoline, which with some two hundred other products, represent the petroleum chemists' contribution to mankind.

The present is to be valued as a day of opportunity for the chemist rather than the high noon of accomplishment. Agriculture requires the help of the chemist more than any other human activity, but the benefit of his work has been tremendously handicapped by the ignorance, isolation, and restricted horizon of the farmer, which makes extremely slow the adoption of new methods and materials, and right here we see wherein the thing called government fails us, for it is hopeless to rely on the individual initiative of the farmer to seek out improvements. Society must place them in his hands for its own benefit, and where government is so ordered that it neither rises to a legislative appreciation of this fact nor could efficiently perform even if it had the appreciation, then it may be justly called an ineffective form of government.

There is an almost untouched field in new agricultural products, the commercialisation of weeds, if you please, such as the sunflower. There is only partial utilisation of potatoes, of cotton, and of wood fibre. We are at the very threshold of the possibilities in the development of new fibres and fabrics. Synthetic rubber still challenges the chemical world. The secret of electrical conductivity is still hidden from man although some progress is reported in the treatment of steel conductors which make them slightly, if at all, inferior to copper. The economic conversion of natural insoluble potash-bearing rocks into soluble potash salts is not yet demonstrated. There is a world of undiscovered country in the conversion of the initial products of the fixation of atmospheric nitrogen, to the myriad nitrogenous substances. Photo-chemistry as yet counts comparatively little in the way of practical accomplishment. And so far in the distance does the production of synthetic foods from inorganic substances appear to be that one does not mention it seriously for fear of being counted irredeemably impractical.

Chemistry will have admirable running mates along the course stretching on into the future. Even the purely mechanical discoveries and developments do not all belong to the past. There is still place in this field, which ordinarily does not challenge the highest scientific attainments, for marvellous performances based on a profound knowledge of physical laws and mathematics. The evidence of this we see, for example, in the Sperry gyroscope; originally an interesting mysterious toy which with twelve years of devoted study and experimentation displaces in a night the magnetic compass, stabilises the ponderous battleship and the feathery aeroplane, and promises to be the agency by which ice-bound ports may be unlocked and kept open to commerce the year round. And far removed from mechanics in the long list of subjects of human interest is the psychopathic laboratory and the Binet-Simon system of analysing—not a physical substance, but the mind of the defective human being, determining the degree of his responsibility to society, and constituting what has been designated as a mental finger-print method of identification of the specific type of mental trouble. The defective and feeble-minded are not only detected at an early age but by prescribing thyroid or other treatment, carefully and persistently given, these cretin children may be grown to normal stature, mentally and physically.

That the genius, devotion, and labours of the chemist may be expressed in valuable accomplishment demands the existence of certain favourable conditions which do not exist at present in this country, and therefore must be brought about. The labourer is worthy of his hire, and, furthermore, unless he receives it he cannot, even if he would, give his labour. One of the greatest discouragements to chemical research work is the absence of any adequate provisions under American law for safeguarding the individual's title to the product of his brain and energy. The patent laws are inadequate to this end. Their first requisite is publicity, and such protection as they do afford is seriously threatened with dissolution by each succeeding session of the National Congress. The average constituent does not distinguish between an odious monopoly which takes from society a right and bestows it upon an individual without recompense to society, and the recognition of a property right in the product of one's brain to be guaranteed for a limited period in return for its assignment to mankind thereafter. The average legislator cannot hold to views nor act upon them beyond the prejudice or insistence of his constituents or he would cease to be a legislator, average or otherwise.

Let us not fail to give adequate consideration to the personal factor. The carrying out of involved chemical processes demands a "feeling," on the part of the workman, that, while it falls short of the fine sentiment of the artist, lifts artisanship almost to the level of art itself. After all, the chemical plant is only a chemical laboratory on a large scale, and we all appreciate, in the laboratory at least, the technique and touch; in other words, a feeling for the work is a necessary characteristic of the operator who expects to gain accurate and successful results.

In countries of modern income a life-long pride and satisfaction on the part of the highly trained chemist in a simple subordinate calling is universal. The mono technic schools of Germany are in the belief of many the chief factor in that nation's unexampled advance in the arts, particularly in the chemical industries. One cannot travel far in chemistry withour coming to Germany. Few branches of the subject can be properly dealt with except we draw examples from Germany. I trust no one here will read into my references to Germany any expression of opinion as to Germany's place in this horrible world tragedy being enacted abroad. We can all meet on the common ground of mourner over the sufferings of the admirable individuals who composed the greater part of every nation. To return to the mono-technic school: it is more then a great economic factor; it represents and examples that unique social principle that sets the German people politically apart from every other nation of the world, the placing of the Fatherland above the individual, the sacrifice of individual opportunity to the principle of the greatest good to the greatest number. There are, as I recall it, over 400 mono-technic schools, and taking the dye schools as an example, the curriculum is of a higher standard than in any save one or two universities in the United States—four years of laboratory practice in neighbouring dye establishments and specialisation in the most involved chemical theory, on the intricate differentiations of the myriad colour compounds and by products, and on the psychology of colour. What American parent would be satisfied to have his son give four years of high-class intellectual effort as a college student and have nothing ahead of him in a long life beyond a foremanship in a dye establishment? And yet this subjugation of the individual has made Germany, in a broad sense, the only producers of dyes in the world and the greatest of dyers.

So we say the day of the Chemist is not to be measured by the personal gain of the chemist so much as by the opportunity for service, and applying to the modest thing the trained analytical mind. So we come back to our original statement, that without devoted personal service many scientific undertakings otherwise possible will prove failures with us. The German estimate of our limitations in this regard is well expressed by the dry comment on the merits of the Diesel Engine—"It works well—except where English is spoken."

There is little appreciation among American financiers, bankers, or the investing public of the value of an idea, and therefore we are without a recognised basis for seeking capital with which to exploit the result of research work, either in the initial stages of the development or for later expansions. The average banker is more impressed with an asset item of buildings, plant, and equipment, even without knowledge as to whether they can be converted to any practical use, than he is with an idea the potential value of which may be substantially unlimited. He will not give value to an idea. There is another obstacle to establishing the value of chemical developments, namely, the absence of any body of recognised consultants whose reports are universally accepted as reliable. The failure to use such men as there are of this type is a handicap to the good project and an imposition always upon the persons whose assistance, financial or otherwise, is sought in the development of a project. No enterprise, regardless of the ability and standing of its sponsors, should be presented in an effort to secure financial co-operation, without being accompanied by a report on the project with conclusions as to its technical and commercial merits from some highly regarded man of scientific attainments.

I would point in passing to another difficulty for which I think the chemist himself is chiefly responsible, and that is that no distinction as to commercial value is made between the bare thought or invention and the developed process or material. Too many chemists view as synonymous the theory which applies to an idea and the processing by which the theory may be converted to practical accomplishment. Chemical theories are innumerable, and of those who present them in the aspect of practical accomplishments there are a vast multitude. I was interested in looking over the report of one of our great mining companies, which maintains a department for the investigation of projects presented for investment. Last year out of 780 projects so presented only 13 were worthy of extended investigation: substantially 2 per cent. I am quite positive that the experience of those engaged in the chemical industries as to new projects which are brought to them by chemists will confirm in this branch of human endeavour as low a percentage of worthy projects as in metal mining.

American problems have been primarily the problems of a pioneer community in a sparsely settled country, where virgin national wealth is to be had by stretching out the hand, where simple direct means backed by energy, daring, and courage accomplish results by main strength and awkwardness. We are going out of that phase of existence into a period where to compete in accomplishment with other nations scientific methods must be employed. The day of the typical "practical man" is passing, and there is dawning the day of the efficient scientific man. The latter is not yet appreciated, he is not generally understood nor honoured. As he grows in public esteem and receives social recognition there will be attached to his ranks more of ability, ambition, and the stronger personalities by whom honour and the consciousness of serving society is more prized than the money wage.

This nation's greatest asset is its thinking men. Our country faces its greatest peril as well as its greatest opportunity. The Day of the Chemist is a day of opportunity for service. It is the blessed privilege of the man of science that his value is measured in proportion to the service he renders society. It lifts him to a plane of nobility unattainable by those who amass even the greatest fortunes without contributing to mankind a comparable return.

But the chemist's most valuable contribution to the world will not lie in the economic value of his process or product. It will come from his moral example and influence. We of this country are not yet awake to the value of truth. I mean the truth that is fact. So little of our national life is ordered on a basis of fact. Contemplate our National legislators, in whose hands are the destinies of this great nation and the waste or the useful fulfilment of our individual lives. One of the most depressing experiences in the life of any observing, thinking American must be the contemplation of the most important and complicated of human activities, government, conducted in an age of scientific approach to every other subject and striving for efficiency in every other activity, without any realisation that such a basis might exist for it. Government with us, like the study of contemporaneous European geography, is largely a matter of personal opinion.

Were some fearful scourge running an unchecked course through the greater part of the civilised world, killing, crippling, and blinding the vigorous youth and middle aged of sixteen nations of Europe, would not the mind and soul of every lover of mankind be enlisted in the service of stamping out the scourge and establishing a quarantine thereafter that would for all time prevent its recurrence? This horrible, unexampled war has been called the Chemist's war—and it is to the honour of any man that he shall do great service for his nation at war, and yet how immeasurably greater would be the accomplishment of any class of men who had contributed something effective to the prevention of war. What will the Day of the Chemist bring forward as his contribution to war's prevention? And yet despite the possession by the German nation of a highly honoured body of the world's greatest scientists the scourge came and none could stay it. Something more then is required than simple devotion to scientific truth. Is it "reasonableness?" In other words, that spirit of mind which is not allied to partisanship—the balanced, considerate, and open mind. When that shall be the recognised mental equipment of every scientific man, then shall dawn the True Day of the Chemist. *Journal of Industrial and Engineering Chemistry*, viii., No. 12.

INSTITUTE OF CHEMISTRY.

Summary of the Revised Regulations Adopted by the Council: July, 1917.

The Studentship. - Every Candidate for admission to the Studentship is required to produce evidence that he is upwards of 17 years of age, and that he has passed an approved Preliminary Examination in subjects of general education. He must also show that, at the time of making application for registration, he is working at an institution recognised by the Council, or under the direction of a Fellow of the Institute in a laboratory or works approved by the Council, with the object of qualifying for the practice of professional chemistry. Registration fee: 5s. per annum.

The Associateship (A.I.C.).—A Candidate for examination for the Associateship is required to produce evidence of having passed an approved Preliminary Examination, and of having complied with the prescribed conditions with regard to technical training and experience set forth in any one of the Sections (*a*) to (*e*) below:—

(*a*) That he has completed four years' systematic day training in the prescribed subjects — including Chemistry, Physics, Mathematics, and one optional subject—at a University or College recognised by the Council, and has passed the class examinations in the said subjects—see *Note* (i.) below; or

(*b*) That he has completed three years' systematic training as above and passed the class examinations, and has had two other years' approved experience* under a Fellow of the Institute, or in a laboratory or works approved by the Council—see *Note* (i.) below; or

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* One year may be accepted by the Council as sufficient where the approved experience in a laboratory or works has been acquired *subsequently* to the prescribed training in a recognised University or College.

(*c*) That he has obtained a degree, including Chemistry in the degree Examination, taken otherwise than in accordance with (*d*) and (*e*) below, at a recognised University, and (i.) has taken a further year's training in Chemistry at a recognised University or College, or (ii.) has had two other years' approved experience* under a Fellow of the Institute, or in a laboratory or works approved by the Council—see *Notes* (i.) and (ii.) below; or

(*d*) That he has obtained a degree with first or second class honours in Chemistry or other diploma recognised by the Council as equivalent after a three years' systematic day course, and (i.) has taken a further year's training in Chemistry at a recognised University or College, or (ii.) has had two other years' approved experience* under a Fellow of the Institute, or in a laboratory or works approved by the Council—see *Note* (ii.) below; or

(*e*) That he has obtained a degree with first or second class honours in Chemistry or other degree or diploma recognised by the Council as equivalent after a four years' systematic day course—see *Note* (ii), below.

Provided in every case that the Candidate has produced satisfactory evidence of training in Physics, Mathematics, and an optional subject, and has passed the class examinations therein.

The Council, however, will consider applications for admission to the Examination for the Associateship from candidates of twenty-seven years of age or over whose qualifications are not in accordance with the Regulations, provided they have passed an approved Preliminary Examination in accordance with the Regulations that they have received systematic instruction, by day or evening classes, in the prescribed subjects, and have passed the class examinations therein; that they have been engaged in the study and practice of chemistry for at least ten years, and provided that their cases are recommended for special consideration by at least three Fellows of the Institute.

In exceptional cases a Candidate may be elected to the Associateship without examination by the Institute. As a temporary measure, and in view of the fact that the war has prevented many candidates from presenting themselves for examination, the Council have made special provision for the consideration of applications from chemists who have served in the navy or army, or have been engaged in other work of national importance.

Note (i.)—Every candidate admitted under the conditions specified in (*a*), (*b*), or (*c*) above—except such as are provided for in *Note* (ii.) below—will be examined in a branch of the Examination for the Associateship to be selected by himself, including a paper of questions relating to the branch selected, and will be examined orally in General Theoretical Chemistry.

Note (ii.)—Any Candidate admitted under (*c*) who has taken a degree with first or second class honours in Chemistry in a recognised University and any Candidate admitted under the conditions specified in (*d*) or (*e*) will be examined in a branch of the Examination for the Associateship to be selected by himself, but will be exempted from the oral examination in General Theoretical Chemistry and from the written part of the Examination for the Associateship, provided that the degree Examination included a Theoretical Examination in the branch selected.

The Examination for the Associateship.—The Examination occupies at least five days, and each Candidate is required to show a *thorough* acquaintance with at least one of the following branches to be selected by himself:—(*a*) Mineral Chemistry; (*b*) Metallurgical Chemistry; (*c*) Physical Chemistry; (*d*) Organic Chemistry; (*e*) The Chemistry (including Microscopy) of Food and Drugs, Fertilisers and Feeding Stuffs, Soils and Water; (*f*) Biological Chemistry, Bacteriology, Fermentation, and Enzyme action; (*g*) Chemical Technology. The fee for the examination is £5 5s.

The Fellowship (F.I.C.)—For admission to the Fellowship, an Associate is required to have been registered for three years, and to have been continuously engaged during that period in the study and practice of Chemistry in a manner satisfactory to the Council and to have complied with one of the conditions following:—(i.) That he has carried out original research of sufficient merit in the opinion of the Council; or (ii.) that he has devised processes or inventions of sufficient merit in the opinion of the Council; or (iii.) in special circumstances, that he is possessed of knowledge and ability equivalent, in the opinion of the Council, to having fulfilled the conditions contained under (i.) or (ii.) above. Entrance fee to the Fellowship £5 5s. Annual subscription (Fellows and Associates) £1 1s.

The regulations, forms, &c., can be obtained gratis from the Registrar of the Institute of Chemistry, 30, Russell Square, London, W.C. 1.

AUSTRALIAN CHEMICAL INSTITUTE.

A NUMBER of chemists in Melbourne having expressed the opinion that something should be done in order to organise on a federal basis those practising the profession of chemistry in Australia, a meeting was convened in Sydney to meet Prof. Masson and discuss the possibility of forming some body having this object. A Provisional Committee was formed, and negotiations opened up with several of the best known chemists in the other States.

At an early stage, meetings were convened in Sydney, Melbourne, Brisbane, and Adelaide, and it was decided that a conference should be called of representatives of each Provisional Committee. The following met in Sydney on Wednesday, January 10, 1917:—Prof. Masson (Melbourne University), Prof. Rennie (Adelaide University), Mr. Henderson (Government Analyst, Brisbane), Dr. Cooksey (Government Analyst, Sydney), and a draft constitution was drawn up, which it was decided to submit to the respective State Committees.

The Provisional State Committees were composed of the following:—

Victoria.—Prof. Masson (Chairman); Dr. W. H. Green; Messrs. P. R. Scott; R. Bean; C. Tilburn; P. G. W. Bayly; M. Bell; R. J. Lewis, Creswell; H. Dowling; G. H. Watson; B. Paton; A. H. Higgin, F.I.C.; E. S. Richards, M.Sc.; A. H. Jackson, B.Sc.; F. E. A. Stone; F. Dunn; A. H. Koch; D. Avery, M.Sc.; V. G. Anderson; A. Douglass; H. W. Levy; J. L. Strevens, Denston; C. S. Dawes; J. Booth, B.Sc.; Power; Ramsden; Dr. F. H. Campbell, D.Sc (Secretary). Secretary's address, 475, Collins Street, Melbourne.

New South Wales.—Dr. T. Cooksey, F.I.C. (Chairman); Profs. C. E. Fawsitt, D Sc., Ph.D.; J. Read, Ph.D.; J. A. Schofield, A.R M.S., F.I.C.; H. G. Chapman, M.D.; Messrs. R. K. Murphy, Dr.Ing.; R. Greig Smith, D.Sc.; G. Harker, D.Sc.; J. M. Petrie, D.Sc., F.I.C.; H. S. Wardlaw, D.Sc.; H. G. Smith; F. B. Guthrie, F I.C.; J. A. Dixon, F.I.C.; T. U. Walton, F.I.C. (deceased); R. H. Walton; L. Meggitt, F.I.C.; F. A. Coombs; R. W. Challoner, F.I.C.; J. D. Granger, Ph.D., F.I.C.; F. L. Watt, F.I.C.; S. Radcliff; B. J. Stuart, B.Sc. (Secretary). Secretary's address, care of Royal Society, 5, Elizabeth Street, Sydney.

South Australia.—Prof. Rennie, D Sc. (Chairman); Dr. Hargreaves, M.A.; Messrs. F. W. Reid, B.Sc.; J. Durward; H. G. Fisher; J. D. Connor, B.Sc.; E. C. Wood, M.A. (Secretary). Secretary's address, 79, Currie Street, Adelaide.

Queensland.—Messrs. J. B. Henderson, F.I.C. (Chairman); H. G. Denham, D.Sc., M.A.; A. B. Chater, Ph.D.; E. A. Derrick; J. C. Brunnich, F.I.C.; R. E. Thwaites, M.A.; A. J. Gibson, Ph.D., M.A.; L. S. Bagster, B.Sc.; A. E. Dawkins, B.Sc.; H. C. Richards, D.Sc.; F. E. Connah, F.I.C.; G. R. Patten; E. H. Gurney; L. A. Meston; T. Parnell, M.A.; W. E. Holmes; G. W. Hargreaves, B.Sc.; T. McCall, F.I.C. (Secretary). Secretary's address, care of Government Chemical Laboratory, Brisbane.

In addition to this, Committees have recently been formed in Western Australia and Tasmania:—

Western Australia.—Messrs. E. S. Simpson (Chairman), I. H. Boas, E. A. Mann, Dr. Steward, Prof. Paterson, Mr. A. O. Watkins, and M. G. Tattersall (Secretary). Secretary's address, University, Perth.

Tasmania. — Communications received from Prof. McLeod and Mr. W. F. Ward (Government Analyst).

The recommendations of the Conference have mainly been adopted by the State Committees with two exceptions which may be mentioned:—

1. The South Australian Committee proposed certain alterations regarding the qualifications for admission, but the New South Wales and Queensland Committees did not agree, and the S.A. Committee has since accepted the Constitution as it stands.
2. The Western Australian Committee has suggested that the headquarters of the Institute be Melbourne, Sydney having been decided upon by the Conference.

Apart from this the points of difference have not been of a fundamental character.

It therefore seems desirable that the Conference originally convened should take steps to put the Institute on a working basis, and the Constitution has been drafted to meet, as far as possible, the wishes of the majority of the States. It is thought that if the modifications referred to above are still pressed by the Committees who proposed them, the machinery exists in the Constitution itself to enable them to be discussed and decided upon.

In order that the permanent officers of the Institute may be appointed, those desirous of becoming members are now called upon to form their State Committees, and appoint their representative on the Council.

Applicants should fill in an attached form, and the same should be forwarded to the Local Secretary, pending the appointment of a General Secretary and the establishment of a permanent Headquarters. At the same time any subscriptions received by the Local Committees should be retained and forwarded to the General Treasurer when he is appointed.

It would be convenient to appoint Local Committees now to hold office until September, 1918.

The names of all officers elected should be sent to B. J. Smart, care of Royal Society, Sydney, who will act as General Secretary, *pro tem.*

(Signed) T. Cooksey,
J. B. Henderson,
E. H. Rennie,
Orme Masson, } Members of Conference.
B. J. Smart (Prov. Sec. for N.S.W.).

June, 1917.

CONSTITUTION.

Sect. 1. *Title.*—The title of the Society shall be "The Australian Chemical Institute." The Institute shall consist of Branches, one of which may be formed in each of the States of the Commonwealth of Australia.

Sect. 2. *Objects.*—The objects of the Institute shall be as follows:—

(*a*) To raise the status and advance the interests of the profession of chemistry.

(*b*) To promote the usefulness and efficiency of persons practising the same.

(*c*) To afford facilities for the better education and examination of persons desirous of qualifying as technical analysts and chemical advisers.

(*d*) To obtain power to grant legally recognised certificates of competency.

Sect. 3. *Membership.*—The following persons shall be eligible for memberspip of the Institute, but in each case admission shall be subject to the approval of the Council:—

1. Graduates of a University of the British Empire recognised by the Council of the Institute, provided that in each case the University course has included not less than three years' study of chemistry.
2. Persons who have obtained an approved Diploma in some branch of Chemistry granted by a Technical College, or School of Mines approved by the Council.
3. Fellows or Associates of the Institute of Chemistry of Great Britain and Ireland.
4. Persons who have satisfied examiners appointed by the Council that they have attained a necessary standard of chemical education.
5. Persons admitted by the Council without examination for special reasons on the recommendation of the Committee of a Branch.
6. Until January 1, 1918, or such other date as the Council may decide, the Institute shall hold no examinations for admission, but the following shall be eligible for admission in addition to those who claim under Clauses 1, 2, 3, or 5:—
   - (*a*) Lecturers or Teachers of Chemistry at an Australian University, Technical College, or Scoool of Mines, or approved Secondary School.
   - (*b*) Chemists who are in charge of a Government Laboratory.
   - (*c*) Chemists who have been in charge of a Laboratory attached to a Commercial or Industrial Establishment for three years.
   - (*d*) Chemists or analysts who have been in private practice for three years.
   - (*e*) Chemists who have been employed for three years in a Laboratory as follows:—
     - University Laboratory.
     - Technical College or School of Mines Laboratory, Government Laboratory.
     - Laboratory attached to a commercial or industrial establishment.
     - Laboratory of a chemist or analyst in private practice.

     Provided that such chemists be recommended by the Chemist in charge of the Laboratory.
   - (*f*) Chemists who have been absent from Australia on War Service may be admitted under Clause 6 without examination after January 1, 1918, at the discretion of the Council.
7. Until the Council and Branch Committees have been elected as hereinafter provided, the power above given to the Council shall be exercised by the Committees now formed in each State and known as Provisional State Committees, each of which shall deal with the applications for membership of persons residing in their respective States. Members thus admitted shall be designated "Original Members."

Sect. 4. *Fellowship.*—The Council shall frame regulations providing for the admission of members to the Fellowship of the Institute.

Sect. 5. *Certificates of Competency in Special Branches of Chemical Practice.*—The Council shall frame regulations for granting such Certificates to members of the Institute by examination or otherwise.

Sect. 6. *Management.*—The headquarters of the Institute shall be situated in Sydney. The management of the Institute shall be vested in a Council and Branch Committees. The Council shall consist of the Presidents of the Branch Committees, together with a General Secretary and a General Treasurer. In the event of any member of the Council being unable to attend a meeting he shall have the right to appoint any member of the Institute to act for him. The General Treasurer and the General Secretary shall be appointed annually by the Council, but for this purpose the General Treasurer and the General Secretary shall not vote. The President of the Branch situated in the State in which the Council is meeting shall act as Chairman of the Council, or in his absence the Council shall elect its own Chairman.

Sect. 7. *Branch Committees.*—Each Branch Committee shall consist of a President, four members, a Branch Treasurer, and a Branch Secretary, who shall be elected annually by the members of the Branch, and shall hold office from September 30 in each year. Any member of the Institute residing in any State shall be a member of the Branch of that State, provided that such member has registered his membership with the Secretary of that Branch, for transmission to the General Secretary. Candidates for election to the offices above mentioned shall be nominated by any two members of the Branch, and such nominations must reach the Branch Secretary not later than August 15 in each year. The ballot papers containing the names of the candidates nominated for election shall be forwarded to the members of the Branch at least two weeks before the Annual General Meeting of that Branch. Members desirous of voting must then erase the names of those for whom they do not desire to vote, and return the ballot papers to the Secretary prior to the General Meeting of the Branch. Two Scrutineers shall be appointed at the General Meeting, to whom shall be handed the ballot papers for examination and report.

Sect. 8. *Duties of the Council.*—The Council shall take all such steps as may appear to it advisable for the purpose of improving the rate of remuneration of Chemists in private practice, or in the employment of Federal or State Governments, or Commercial Establishments. The Council may appoint Committees for any special purpose considered likely to benefit the profession of chemistry (as, for instance, the fixing of standard methods of chemical analysis, the publication of memoirs or bulletins, the standardisation of fees for professional work, &c.). The Council shall keep before it the desirability of obtaining a Charter, and at the proper time take all necessary steps to attain this object.

Sect. 9. *Duties of Branch Committees.*—The duties of the Branch Committees shall be as follows:—

(*a*) To advise the Council in matters appertaining to the admission of new members to the Institute.

(*b*) To convene local meetings of members of the Institute, from time to time at its own discretion, or on requisition by ten members of the branch, to discuss matters affecting the interests of Chemists, and to transmit the resolutions of such meetings to the Council.

The Branch Committee shall convene a General Meeting of the Branch for a special purpose upon a requisition to that effect signed by not less than ten members of the Branch.

(*c*) An Annual General Meeting of each Branch shall be held during the month of September in each year.

Sect. 10. *Accounts.*—

1. Membership and examination fees received by each Branch must be sent in to the General Treasurer of the Institute.
2. All moneys except a sum authorised by the Treasurer for petty cash expenses shall be deposited at a bank approved by the Council, when payments therefrom of all accounts that are certified as correct by the Council shall be made by cheque on such bank signed by any two of the following persons:—The General Treasurer, the General Secretary, and the President of the N.S.W. Branch.
3. A suitable allowance, proportionate to membership, for expenditure on postage, stationery, and petty cash, shall be granted annually by the Council to each Branch. Other expenditure by any Branch, such as salaries of Officers, rent of office, &c., shall not be incurred without the consent of the Council. The Council may, however, on the application of any Branch grant funds for office or other expenditure in that Branch.
4. Any Branch may raise funds by special subscription from its own members and expend them on the work of the Institute in that Branch.
5. Accounts are to be kept by local Treasurers of all money received and expended by them, and such accounts must be passed at a meeting of the Branch Committee and certified by the President of that Branch. A return of such expenditure, accompanied by the receipts for each disbursement, shall be sent to the General Treasurer every six months. The final return for the year must reach the General Treasurer not later than July 20.
6. The Council shall forward to the Branches each year during the month of August a statement of the financial position of the Institute. This statement shall include all details of expenditure incurred by the Branches.
7. The financial year shall close on June 30.

Sect. 11. *Subscriptions and Fees.*—The subscription of each member of the Institute shall be one guinea per annum payable in advance on July 1 in each year. Any member whose subscription is not in arrears may at any time compound for his subscription for the current year and all future years on payment of such sum as will, together with the annual fees already paid, make a total sum of twenty guineas. Any member on his joining may compound for life on payment of fifteen guineas. Any member whose subscription shall be twelve months in arrears shall forfeit all the privileges of the Institute, and the Council, after having given due notice shall be empowered to remove the name of such member from the lists of the Institute. After January 1, 1918, the Council shall have the power to fix an entrance fee and fees for examination for admission to the fellowship and for certificates of competency.

Sect. 12. *Unprofessional Conduct.*—The Council, after due enquiry, shall have the right to expel from the Institute, or otherwise penalise, any member who may have been guilty of disgraceful conduct in a professional respect or other offence, which, in the opinion of the Council, renders him unfit to be a member. Proper notice of an enquiry held under this section shall be given to such member, who shall be entitled to be present and to be heard at the enquiry. The secretary shall give him notice of the decision and the Council shall report such expulsion or other penalty to the Branch Committees for transmission to the members at their Annual General Meeting.

Sect. 13. *Alteration of Rules.*—The Council may at any time submit a proposal for the alteration of any of the Rules to the Branch Committees for consideration and report, and if the whole of the Branch Committees signify their assent such alteration shall take effect. If any Branch Committee dissent from such alteration or desire to propose an amendment to the same a referendum to the whole of the members of the Institute shall be taken, whose decision shall be final.

NOTES AND QUERIES.

, Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Metallic Cerium.—I should be much obliged for the address of some professor who will favour me with a practical consultation on the industrial preparation of anhydrous chloride of cerium starting from the hydrated chloride, and on the electrolysis of fused chlorides—or, in a word, on the modern fabrication of metallic cerium.—L. Vecchi.

THE CHEMICAL NEWS

Vol. CXVI., No. 3019.

THE METALLURGY OF THE RARER METALS.*

By J. W. RICHARDS.

There are many metals which may be called "the rarer metals." Among them the most interesting by far, to the metallurgist and to the economist, are those metals whose compounds are relatively cheap but which command a high price because of the difficulty of their reduction. These are the metals whose market price may at some time be reduced one-half, three-quarters, perhaps nine-tenths, by improved methods of reduction, and the discussion of how this might be accomplished and to what uses these metals at such low prices might be put, is interesting to the border of fascination.

If this article were being written thirty years ago, aluminium would be one of the metals to be discussed. It is now out of that class, but in 1886 it was one of the rarer metals, selling at 10 dols. per lb., although its ores were "as common as dirt." At that time you could buy a ton of bauxite ore containing 0·6 ton of alumina or 0·3 ton of aluminium, for 5 dols., while the 0·3 ton of aluminium was being sold for 3000 dols., at wholesale. Or, eliminating the purely chemical work, 0·6 ton of chemically purified alumina could then have been bought for 50 dols., while the aluminium it contained was worth on the market 60 times that amount. Such were the metallurgical conditions in the aluminium industry thirty years ago, and so attractive were they to experimenters and inventors that the genius of the profession expended its best talents on the problem, with the result, in less than ten years, of reducing the market price to less than one-tenth its former figure.

The silicon industry furnishes another example in point. Silica is the most abundant and the cheapest material in nature, yet silicon was selling in 1900 as a chemical curiosity at *over 100 dols. an ounce*. Imagine the stirring up which my metallurgical wits received, when in 1902 Mr. Tone, at Niagara Falls, showed me a barrel full, 100 lbs. perhaps, of silicon made in his electric furnace, and asked me what uses it could be put to. At the present time 10 c. per lb. is a good market price for silicon, which is often sold by the carload.

It is such seeming fairy tales as these which constitute the fascination of those metals which are abundant in nature but whose high cost rests on the difficult and costly methods of reduction employed. Such opportunities exist for our rising generation of chemists and metallurgists to make themselves famous and, incidentally, rich—but they will find their fame more of a reward than their riches.

Among the metals at present of high price, but which by improved metallurgical processes might be made very cheaply, are beryllium, boron, magnesium, calcium, strontium, zirconium, molybdenum, barium, titanium, chromium, and cerium (mixed metals of the cerium group).

Beryllium.

Commencing with one of the light, alkaline-earth metals, its ore is not so rare as is ordinarily supposed. Most non-mineralogists link it with beryl, and think of the latter as a very pretty and very expensive gem—the emerald. But the emerald is only the clear green or aquamarine stone, while massive beryl, looking like massive green quartz, is much more common, and is even abundant in some localities. The beryl crystals of Acworth, N.H., are sometimes as large as a barrel, and the massive beryl at this locality is quarried like felspar. Its composition is: SiO_2, 67; Al_2O_3, 19; and BeO, 14 per cent.

It is difficult to say what the price of this material would be if it was desired by the ton, but it should not be expensive. When chemically treated, both the Al_2O_3 and the BeO which it contains could be separately obtained.

Up to the present no one has succeeded in isolating the metal except by reducing a halide salt of beryllium by potassium or sodium (Bussy, Wöhler, Debray, Menier, Reynolds, Nilson and Pettersen, Kruss and Moraht), or by electrolysis of double chloride, bromide, or fluoride of beryllium and sodium or ammonium (Borchers, Warren, Lebeau, Liebmann).

These methods are tedious and costly for two reasons. First, they require the conversion of the beryllium into an anhydrous halide salt, which is a difficult chemical operation; second, the electrolysis sets free the halogen, which is very destructive to electrodes and apparatus. It is not to be expected that beryllium can be made cheaply until someone masters the direct electrolysis of the oxide, dissolved or suspended into a more stable melted salt. This is by no means an impossibility; a similar solution was found for the aluminum problem, and systematic, determined search would in all probability find the answer for beryllium. In such a case, the cost of the metal would depend only on the cost of beryllium oxide, being probably not more than 20 c. per lb., plus the cost of the oxide. Since BeO is only 36 per cent Be, it would require 3 lbs. of oxide to give one of metal; if the oxide cost 10 c. per lb., the total cost of the metal should not exceed 50 c., by such a suppositious process. Dealers in rare chemicals will charge you, at present, 300 dols. per oz. for a specimen of it.

Lebeau has produced beryllium bronzes by reducing directly, in the electric furnace, a mixture of beryllium oxide, copper oxide, and carbon: 0·5 per cent of beryllium makes copper hard and sonorous, 1·5 per cent makes it yellow, and 5 per cent makes a fine, golden yellow bronze.

Beryllium, like any other rare metal, must find uses which justify its cost. Being white, malleable, and unchanged in air, its specific gravity, 1·64, would make it particularly useful for objects where great lightness and permanence in air is the first consideration and cost secondary. So far we practically know nothing about its tensile strength or rigidity, about how it might be strengthened or stiffened by small additions of magnesium or aluminium or even of zinc, or copper, or manganese, or some other metal. We do not yet know the mechanical properties of its fine bronzes, except that they are somewhat similar to aluminium bronze, but in what respects they might be superior or perhaps unique is unknown. Finally, the metal may easily possess special properties, now unknown, which may render it particularly useful for some specific purpose. Its specific heat, for instance, is the highest of any useful metal, and its latent heat of fusion must be abnormally high, possibly 300 calories, and its latent heat of vaporisation probably higher than that of any known element, except carbon or boron. Such characteristics might give it special uses in electrical instruments, or for physical apparatus, where its cost would not exclude its use. Altogether beryllium is a metal which will well repay extended metallurgical research and minute physical and chemical study of its many unique properties.

Magnesium.

The metallurgist has been coquetting with magnesium for half a century, and has not, as yet, made a fraction of the progress which he should have made. We can get its oxide cheaply and in abundance, its salts are not very difficult to prepare, we know their properties to a considerable extent, we know almost all the properties of the metal which bear on its isolation, and yet the industry lags and halts as if there were no such thing as modern metallurgy. To prepare by tedious methods the anhydrous double chloride, and then to electrolyse it about as Matthiesen did fifty years ago, is nearly all that can be said with certainty about its present metallurgy. At an rate, using magnesium oxide costing a few cents per lb., the metal sells for about as many dollars per lb., and yet there is a great scarcity of the metal.

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* Presented at the 8th Semi-Annual Meeting of the American Institute of Chemical Engineers, Cleveland, June 14, 1916. From the *Journal of Industrial and Engineering Chemistry*, viii., No. 8.

Dr. W. M. Grosvenor, in a recent paper before the American Electrochemical Society, summarises the present methods of production and the uses of the metal. Happily he also suggests the great field open for improvement, especially for radically new metallurgical methods of production. With magnesium in its salts costing less than 8 c. per lb., he places the actual cost of the metal at 1·00 dol. per lb., leaving over 90 c. per lb. for the cost of its extraction. "Brethren, these things ought not so to be." Speaking with the enthusiasm born of past achievements in electrometallurgy, along entirely analogous lines, a modern, up-to-date attack on this problem ought to result in producing magnesium at 25 c. per lb.

The point of attack should be undoubtedly to reduce the oxide directly. The halogen salts are hygroscopic, and the halogen is destructive of the reducing apparatus. It is almost certain that proper research will enable the electrometallurgist to feed magnesium oxide (MgO) directly into an electrolytic bath of fused salts, and take magnesium or magnesium alloy from it. The pure metal will float on almost any fused salt, but its alloy with heavier metals may be made such as to sink, and many of its alloys have immediate useful applications.

Dr. Grosvenor makes suggestive remarks about the reduction of magnesia by carbon. If the boiling point is only 1200° C., then a process of reduction similar to that of zinc oxide might be practicable if we could (1) find a retort material which will stand the temperature required (1800 to 2000° C.), and (2) condense the vapours without contact with air. Fortunately, magnesium does not form carbide at high temperatures, so that its reduction is simpler by that much. Dr. Grosvenor speaks of a chemical process which will use cheap raw materials, a moderate amount of fuel, and give a fair efficiency of reduction. With all expenses added, he estimates a cost not over 35 c. per lb. This may be true, but whether it materialises or not, he and his colleagues have the right vision of the possibilities, I may even call them the probabilities, of this field; they are truly "absolutely fascinating."

While the world war lasts, with its enormous demand for magnesium for military purposes, the price will remain in the dollars per lb. But experience in this line is being rapidly accumulated, and improvements are undoubtedly rapidly succeeding each other, although keen competition is keeping them secret as far as possible. After the war's close, with normal industrial conditions reappearing, magnesium will undoubtedly sell at a price which will take it out of the class of the rarer metals and put it among the common ones. As the price goes down its industrial uses will increase in geometric proportion, and instead of production being expressed in thousands of lbs. per year it will reach thousands of tons. This will be another of the by-products of the great war's stimulus to metallurgical industry.

The possibilities held out to the metal industry by reasonably cheap magnesium are extremely interesting. The stiffening of magnesium to produce strong alloys with specific gravity not over 2 has not been properly studied. It is quite possible that alloys analogous to *Dur-alumin* may be discovered as strong as soft steel and only 30 per cent of its weight, which will find extensive use in aeroplanes and dirigibles. Such alloys may also largely displace aluminium alloys, which are used by thousands of tons annually in the automobile industry, with a saving of one-third in weight, which will compensate for a higher first cost. The metallurgical uses of magnesium will also be greatly extended by its lower price, such as for deoxidising brass, bronze, nickel, and Monel metal, since it is a much stronger deodoriser than aluminum. In fact, aluminum has blazed the way into numerous uses for which magnesium, as soon as it becomes cheaper, will compete and replace its older sister. With supplies of magnesium ore as plentiful as those of aluminum ore, and the metallurgist awake to his responsibilities and producing the metal cheaply, there will inevitably be a large future for magnesium as one of the common metals of every-day life.

Calcium, Strontium, Barium.

These form a trio of highly interesting elements common enough in nature, but all scarce and of high price because of the metallurgists' lack of efficient and cheap methods of reduction. With burnt lime, CaO, one of the cheapest of common materials, strontium sulphate, a mineral found in considerable abundance, and barium sulphate, so common as heavy spar that it is used as an adulterant for some cheap paints, the metallurgist is again faced with the demand for cheap methods of reduction. And yet, although calcium is sold at a few dollars per lb., strontium and barium cost several dollars per oz. Here is a two-fold need: *First*, cheap production; *second*, a thorough study of these metals to find out their specific properties and their particular uses. Which should be undertaken first is an interesting topic for discussion. Historically, the metallurgist has usually produced the metal first and then studied its properties and possibilities; at present, with these metals already at hand, metallurgical activity might be greatly stimulatad by extensive studies of the properties, alloys, and chemical uses of these elements. Our present information in this direction is fragmentary and partly unreliable as far as it goes. A Carnegie research scholar, or even the Bureau of Standards, by disclosing to us some of the unknown properties of these elements, might stimulate the experimenter to renewed efforts to find cheaper methods of reduction.

Calcium, at the present time, is the best known of these three elements. The method of electrolysing its fused chloride and lifting the metal away from the surface, as an irregular stick, has been fairly successful, and since the chloride is not difficult to dehydrate, the whole operation is not very expensive. Calcium is therefore at present perhaps a *semi-rare* metal, which could be produced much cheaper even by present methods if made on a large scale to fill a large demand. The method of production is easily susceptible of minor improvements and the chlorine is a valuable by-product to the manufacture. The principal hitch at present is in finding the uses for a large production of calcium. Here is where extensive study of the properties and possible uses of calcium would greatly stimulate the metallurgical industry. With a specific gravity of 1·85, its possible alloys with other light metals should be exhaustively studied; quite possibly some of them are strong, resistant to air and water, perhaps even to acids. Calcium tarnishes easily in the air, and magnesium also, but it is quite possible that some alloy of the two does not tarnish, and may have valuable mechanical properties. Another large possible use is as chemical purifying agent in melting and casting metals. Calcium-silicon-aluminiom alloy has already found application as a deoxidising agent in steel, because while aluminiom oxide and silicon oxide and their combination with each other are infusible at steel-smelting temperature and therefore are eliminated slowly from the metal, calcium oxide forms with these an easily fusible slag, which easily rises out of the molten metal. It is quite possible that a small addition of metallic calcium may in a similar manner reduce the amount of sulphur and phosphorus in steel, because it is either as calcium sulphide or calcium phosphate that these elements are eliminated in refining steel. Other metals and alloys, whose properties are damaged by sulphur or phosphorus, may be similarly refined or improved. The alloys of calcium with copper, tin, bronze, brass, Monel metal, and other commercial alloys have not been studied; until they are, no one knows how many useful mixtures may exist with particular properties of industrial value. The question of adding calcium to the light, stiff aluminium alloys, for instance, is worthy of attention, but has not been touched.

Strontium is a silvery white, very soft metal, with properties similar to calcium, density 2·54. Its ores cannot be called rare minerals, and it is a rare metal, therefore, only because of the difficulty of its isolation. It is chemically very active, and electrochemically extremely hard to manage. It has about the same specific gravity as its fused salts, so that it neither rises nor sinks in any of them quickly; it seems also to redissolve in its melted salts with great velocity, so that very high current density is required to obtain any metal at all. Its surface tension appears to be abnormally high, so that it separates out in more or less minute globules which are highly indisposed to running together into one mass. What an attractive subject this forms to the electrochemist who really wants to meet difficulties and taste the joys of overcoming them! And then, one may well ask: "To what purpose?" Here again we do not know, but we can feel confident that in the innumerable list of possible combinations of metals strontium might have properties different from any other element, which would lead to its employment on a large scale. These are all questions of the future which form the undiscovered country open to the investigator and chemical pioneer. We may well thank our stars that the world of science still holds unexplored areas to tempt the adventurous investigator and to reward the *wanderlust* of the metallurgical pioneer.

Barium is common in its compounds and almost unknown in itself. Under electrolytic conditions where calcium comes out *en masse*, and strontium separates as small globules, barium is obtained only as a fine powder. Its density is 3·75, but its salts are heavier than the corresponding strontium and calcium salts, so that the fine powder may sink or swim, largely according to the temperature. And yet the fused barium salts are very decent and manageable salts, easily obtained anhydrous and melting cleanly. Their electrolysis, however, is nearly the most difficult task that the electrometallurgist can take up. But it should be taken up and mastered, because a metal so common in its compounds could be obtained in large quantities if uses for it were developed, and if our modern electrometallurgists are worthy successors of Faraday, Bunsen, and Castner, they should vigorously attack the problem of its cheap extraction. Even if their end was not reached, they would be whetting their metallurgical wits upon the finest of chemical whetstones, and their experiences would be of value to themselves as well as to other lines of electrometallurgy.

(To be continued).

NITROGEN AND NITRATES FROM BITUMINOUS COAL.*

By C. G. ATWATER.

Every few years a wave of nitrogenous famine seems to sweep over the daily press, arousing more or less interest and apprehension on the part of the public. Coincident with these waves, discoveries which remove the danger of famine and therefore deliver posterity from the prospect of perishing of starvation, are brought to public view.

Some eight or nine years ago Sir William Crookes sounded a "note of alarm" and our deliverance by the recovery of atmospheric nitrogen through the electric arc was predicted. A few years later commercial cultures of nitrogen-fixing bacteria were discovered, and their beneficial activities were greeted with more or less journalistic and public enthusiasm. The *New York Tribune*, commenting editorially on the appearance of electrolytic fixation and of the nitrogen-fixing bacteria at that time, proclaimed its entire willingness to credit the inventors of either process with the preservation of our descendants from death by hunger, but admitted its inability to give both credit for the same beneficent work.

I have not seen in the public prints any widespread announcement of the fact that the recovery of nitrogen from bituminous coal is destined to save future generations from starvation, but in view of the fact that this process has always had and still has as great a promise as either of the others and is much closer to our ordinary manufacturing operations and industrial organisation, I feel that such a proclamation may be expected at any moment. While there is an attractive touch of romance in the idea of converting the atmosphere into food, even though somewhat overworked of late, it must be remembered that, even in the legend, the rainbow was in the air while the pot of gold had to be dug out of the ground at its foot.

These circumstances furnish me with some shadow of excuse, at least, for this paper. Additional colour is given to this excuse by the fact that the immediate demand of nitrogen for producing food for the preservation of life is supplemented by a dire need for it in the production of explosives to be used in quite the opposite direction. It might be interesting, but would probably be quite useless, to speculate as to whether these two needs could not be so manipulated as ultimately to neutralise each other in the outcome.

Ammonia from Bituminous Coal.

In speaking of the potential amounts of ammonia recoverable from bituminous coal, as has been done for years past in the public prints, it has been the habit to limit such speculation to the amount of coal actually made into coke. There were at least two good reasons for this, one being that this coal was already being subjected to the process of destructive distillation, and hence was commercially eligible for treatment by the by-product recovery process. A second was that the amount of ammonia recoverable from the coking operation was until recently so far in advance of the amount actually being recovered, the ratio being about 4 to 1, that any argument for conservation or contrast with European practice could be sufficiently enforced with this simple illustration without going further afield. Such statements, so far as I have been guilty of them, erred only on the conservative side. They limited themselves to the replacement of beehive coke, used almost exclusively in iron smelting, with by-product coke. They took no account of the extremely probable increase in the iron industry and they passed by, in rather a cursory fashion, the immense production that would ensue if even a moiety of our ordinary fuel consumption were conducted with by-product recovery. A little closer examination of the actual conditions will show how important these omissions were.

In order to get the data in proper sequence, I will first state the present figures. The ammonium sulphate production in the United States for the year 1915 is estimated at 220,000 net tons, figuring all forms of ammonia as sulphate. The largest amount of coal made into coke in any one year, as reported to date, including beehive, by-product, and gas-house coke, was in 1913, and amounted to over 73 million tons. This should have yielded over 700,000 tons of ammonium sulphate. In other words, the maximum recovery is a little less than one-third of the maximum amount possible. It is highly probable, however, that the year 1916 will increase the total figures, though it may not change their ratio. The beehive coke production for the past half year, if maintained, will give the largest year on record, and the same is true of the by-product coke output. An increase of 25,000 to 50,000 tons of ammonium sulphate for the year is considered probable. There are estimated to be 2600 new by product coke-ovens actually under construction, and 1100 more that have been definitely decided upon. These will add about 15,000,000 tons of by-product coke to the annual capacity when completed, so that within two years an output of 375,000 to 400,000 tons of ammonium sulphate per year is quite possible if business conditions favour complete operations.

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* Paper read before the American Chemical Society, New York City, September 25—30, 1916.

The output of bituminous coal for the year 1915 was 438,550,000 tons, and the Geological Survey's estimate for 1916 is 500 million tons. If we figure a recovery of 1 per cent in ammonium sulphate this would amount to 5 million tons per annum. All of this ammonia is recoverable, and all but the modicum recovered is now wasted. The first objection to this statement that will occur is, of course, the difficulty of recovering by-products from the simple furnaces in which most of this coal is consumed. These difficulties are by no means so great as has been popularly accepted, and a notable amount of progress has recently been made along the line of substituting methods of fuel treatment that permit of ammonia recovery.

In the first place a great deal of coke is now being used in place of anthracite coal. The latter has constantly risen in price, and its production is decreasing. In many districts of the Middle West, coke has taken its place as a smokeless fuel. There are a number of coke-oven plants which regularly turn a respectable portion of their output into domestic coke, and this business is steadily increasing. Domestic coke is regularly distributed from the coke plants at Chicago, Ill., Milwaukee, Wis., Duluth, Minn., St. Louis, Mo., Muncie and Indianapolis, Ind., Hamilton, Ohio, Detroit, Mich., Glassport, Pa., Geneva, N.Y., Everett, Mass., Camden, N.J., and is obtainable in many other cities. Some domestic coke will also be supplied to the local market from the new plant now building near Newark, N.J. These conditions are emphasised by the fact that there is no prospect of any diminution in the price of anthracite, nor is it to be expected that the present burners of smokeless fuel will ever return to the former smoky and undesirable conditions.

An additional impulse in this direction is the increasing domestic and industrial consumption of gas. Large areas of the Middle West have been accustomed to natural gas at a low price. The supply seems to be finally on the wane and it is only a question of time when this territory will have to be supplied with artificial coal-gas, which will necessarily be made with the recovery of by-products, including ammonia, or for industrial uses, with producer gas, which may well be made with by-product recovery. Some years ago much was expected in the way of ammonia recovery from bituminous coal by the agency of the Mond gas producer. The expected development in this direction did not take place. Certain drawbacks stood in the way of its wider introduction, and its coadjutor in power development, the large gas engine, found difficulty in competing in cost of installation and operation with the steam turbine. Later developments in modified forms of the Mond producer, as in the Lymn type of apparatus, have brought about the introduction and successful commercial operation of a number of such ammonia and power-producing plants in Great Britain, and in Germany, Italy, Spain, China, and Japan as well. There is good reason to believe that progress in this country in this direction will not be much longer delayed. It must be noted in this connection that the ammonia recovery from coal treated in these producers is approximately *four times* as great as in the by-product coke-oven. With our accepted practice of concentrating power generation in large central stations, there is good reason for considering this development as an immediate commercial possibility.

Another reason for an increased use of ammonia from bituminous coal is the low cost of production, compared with the electrolytic or synthetic processes, when necessary transportation costs are included. The advantage that coke-oven ammonia has in this respect been stated frequently, and by various acceptable authorities, and so far as I know this has never been contradicted by anyone even approximately without bias. It therefore seems of little use to set up a man of straw in order to overturn him. Coke-oven ammonia, being recovered as a by-product of the main product, coke or gas, is produced with but minor regard as to the demand for it, hence must be sold for the best price obtainable. Therefore, in any event, the argument for it, in view of the existing coke industry and undertakings, would probably partake of the nature of a request to "Come on in, the water's fine!" Certainly a statement that ammonia could be made more cheaply on a commercial basis by resort to water-power development would hardly seem to be an adequate reason for asking the Government to lend financial aid to such an enterprise, more particularly when such a project includes the making of fertilisers in times of peace, as well as explosives in war. There are a half-dozen other good reasons why coke-ovens are our best source of ammonia, in peace or war—geographical distribution, immunity from enemy attack, speed with which new units can be erected, production of other essential materials, conservation of natural resources—I cannot stop to go into them all, more especially as they have been adequately covered elsewhere. (See paper "Ammonium Sulphate as a Source of Combined Nitrogen," by J. W. Turrentine, *Jour. Ind. Eng. Chem.*, 1916, viii., 584; H. Koppers Company, Pittsburgh, Pa., Pamphlet, May, 1916; "Position of Gas Industry in the Nation's Scheme for Preparedness," by W. H. Gartley, *Gas Institute News*, 1916, v., 302; paper "Sources of Nitrogen Compounds in the United States," by Chester C. Gilbert, Smithsonian Institution, June, 1916).

Transformation of Ammonia to Nitric Acid.

The oxidation of ammonia to nitric acid is practically a new process in this country. Commercially, its prospects seem to offer little attraction, as the ordinary method of producing nitric acid by treating sodium nitrate with sulphuric acid is a less expensive one. Its principal functions would be in time of war when sodium nitrate would possibly not be obtainable.

As the great resource of this country for combined nitrogen lies in the recovery of ammonia from bituminous coal, the adaptability of this form of ammonia to oxidation by the Ostwald or some other process is most important. The Ostwald process, as is well known, depends upon the action of a catalyst on a mixture of ammonia and air, or air and oxygen, such catalytic action being more or less subject to derangement or poisoning by certain impurities. Granted that the Ostwald process is capable of producing nitric acid from ammonia in large qantities, which in view of the present European experience we may safely assume, the question resolves itself into an investigation of the effect of the impurities and the process of their removal if necessary.

That the impurities in coke-oven ammonia can be successfully removed so as to deliver a gas that is to all intents and purposes pure, has been amply demonstrated. This is regularly done in the manufacture of anhydrous ammonia, aqua ammonia, and ammonia for the production of pure ammonium salts. The methods employed it is not necessary here to describe. It is probably possible to modify these methods for the purification of ammonia for oxidation on a scale of, say, one hundred tons per day, at a reasonable cost, and what modifications, if any, are permissible in order to lessen this cost without interfering with the practical operation of the catalyst, are problems that can be solved only by diligent experimentation on a laboratory and on a factory scale. In addition to the successful work which has unquestionably been done abroad, such investigations have been recently undertaken by several different agencies in this country and considerable progress has been made. From one source of unquestioned authority I am authorised to make the following statement:—

"Independent laboratory investigations have definitely shown that we can purify coke-oven ammonia on a commercial scale quite well enough to permit satisfactory oxidation to nitric acid. The expense of purification is well within reasonable limits, and the experiments indicate that there is no practical obstacle to the use of coke-oven ammonia for nitric acid manufacture. Definite statements on this point are withheld until an actual commercial demonstration can be made."

As further evidence of the practicability of the oxidation process, I am indebted to Mr. Lewis A. Riley, of New York City, for the following brief statement of the Ostwald process for the oxidation of coal ammonia to nitric acid:—

"In the year 1900 Prof. Ostwald made arrangements to carry on his experiments with the Central Station for Scientific Technical Investigations in Neubabelsberg, near Berlin, which was an Institution supported by a number of explosive works in Germany to undertake industrial investigations and work out technical processes. These experiments were under the general direction of Herr Geheimrath von Duttenhofer of the Rottweiler Explosive Works. Before the conclusion of this experimental work in the year 1903 Herr von Duttenhofer died, and his successor abandoned the work in an nnfinished condition.

"The Chemical Works Griesheim-Elektren next interested themselves in the matter and carried on some experimental work in which the previous apparatus from Berlin was used.

"In the summer of 1904 official tests gave only 70 per cent conversion efficiency, which appeared insufficient for commercial success. This led the Griesheim Works to abandon the experiments, although immediately subsequent to these tests the cause of the low yield was discovered and remedied, it being found that the platinum contacts required more frequent changing.

"The process was then taken up by the Gewerkschaft des Steinkohlenbergwerks Lothringen at Gerthe, near Bochum, and in 1906 a small plant was put down and operated there, which gave a conversion of 85 per cent, on which results the Lothringen Company decided to proceed with the building of a large plant.

"The construction of this large plant was badly handled and resulted in some unfortunate litigation, owing to the constructing engineers and manufacturers having departed from the designs and specifications in certain parts, and some of the auxiliary apparatus gave considerable trouble.

"The plant was in certain respects rebuilt, and although the first cost of the plant was on this account considerably higher than should have been the case, it was, nevertheless, satisfactorily completed in 1908, and since December of that year it has operated continuously.

"Sometime during the year 1910 the operation of this plant was carefully investigated and tested by the Nitrate Products Company, Ltd., of London, and was purchased by this company, which is understood to be closely affiliated with the cyanamide interests. The purchase was made based on this investigation and tests which were stated to show a conversion efficiency of 85 per cent on the basis of ammonia to nitric acid, corresponding to the tests of the experimental plant of the Lothringen Company, and on which the latter company originally accepted the process.

"The plant since beginning operations in 1908 down to a period just preceding the present war had operated practically continuously, using coal-ammonia from the Bochum coke-ovens for the production of nitric acid. The nitric acid produced was then used for the further absorption of additional ammonia in the production of commercial ammonium nitrate, which has been disposed of on the market as such. This plant and process was, therefore, developed and perfected in the use of coal-ammonia as the nitric acid raw material, and its success on this material was thoroughly demonstrated both by the operations conducted by the original owners, the Lothringen Company, and subsequently by the Nitrate Products Company.

"A further development of this plant and process has been its application to the oxidation of cyanamide ammonia, and it is understood that the second plant built for the commercial oxidation of ammonia, which was located in Belgium, was designed for the utilisation of cyanamide-ammonia.

"Test figures of the operation of this plant for a 20-month period show 83 per cent nitric acid conversion with 97 per cent ammonia absorption.

"The ammonia oxidation process has, since 1910, been controlled by the Nitrate Products Company. It is understood that its application by this company has been restricted to the oxidation of cyanamide-ammonia, although the Gerthe plant was being successfully operated on coal-ammonia up to the start of the present war."

To this statement I may add that, according to Lunge ("Coal-tar and Ammonia," 5th ed., 1916, 1572), on the authority of the Deutsche Ammoniak-Verkaufs-Vereinigung, the sales of ammonium nitrate produced by the Ostwald process at the Lothringen plant were as follows:—651 tons in 1908; 1096 tons in 1909; 1237 tons in 1910; about the same in 1911. All these amounts and the subsequent production to the opening of the war are to be credited to coal-ammonia.

In conclusion, I may cite the following summary, from the last edition of Lunge, which carries additional weight, coming as it does from Central Europe, where they have produced more ammonia from coal, and more from the atmosphere, and have transformed more of it into nitric acid, than in any other country:—

"The synthetical production of ammonia from atmospheric nitrogen must find its limits in the impossibility of producing the requisite enormous amount of electrical energy *in infinitum*, whether by water-power or otherwise. As far as we can look forward, the principal source of ammonia will be always the nitrogen of coal, just as this as been the case for a long time past in the case of the comparatively small fraction of coal consumed for the manufacture of illuminating-gas, and more recently by carrying out the coking of the coal in such a way that the formerly lost by-products, ammonia and tar, are recovered. This last proceeding is sure to be more and more extended. Even the general conversion of the coal to be used for heating, into gaseous fuel, with recovery of its nitrogen in the shape of ammonia, is within visible distance."—*Journal of Industrial and Engineering Chemistry*, viii., No. 12.

AN ANALYSIS OF THE THEORY OF GELS AS SYSTEMS OF TWO LIQUID PHASES.*

By EMIL HATSCHEK.

The most generally accepted theory of the constitution of coherent gels like gelatin or silicic acid gels is that they consist of two liquid phases having an interfacial tension (Wo. Ostwald). Although this assumption leads inevitably to certain consequences, no attempt has so far been made to examine these consequences mathematically. The object of the following analysis is therefore to ascertain whether the theory of two liquid phases is compatible with the elastic properties of gels, which have been experimentally determined by various investigators.

It is well known that gels retain constant volume when deformed, and this behaviour is, of course, what would be expected of bodies consisting substantially of liquid, although it is not necessary that they should be composed of two liquids to exhibit it. If this should be the case, the gel must necessarily have a cellular or polyhedral structure; *i.e.*, it must consist of polyhedra of one phase approximating as much as the conditions permit to spheres, separated by thin films of the other phase. If such a structure is either stretched or compressed, the internal surface must be increased, since the polyhedra in the unstressed state are minimum surfaces, and surface energy must be produced. This surface energy is necessarily the only source of the apparent elasticity, since there are no other forces possible tending to restore the original shape of the system.

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* A Paper read before the Faraday Society, May 9, 1916.

We can therefore assume a polyhedral structure and determine how the surface increases when it is stretched or compressed. The surface so produced must be proportional to the work done in producing the elongation, and from this equation we can calculate the stress necessary to produce a given deformation. It is then possible to compare the stress-deformation curve thus obtained with the experimental results available.

As regards the geometrical form of the structure, it will obviously be the safest course to assume that it consists of equal polyhedra of one kind, which fill space completely. Of these there are two—the rhombohedron (with the cube as minimum case) and the rhombic dodecahedron, which is, of course, the most probable element of structure for obvious reasons. The calculations have been carried out for both cases, assuming the direction of stress to be one of the principal axes, and lead to expressions which are naturally rather inconvenient for the further mathematical treatment. By plotting the curves for elongation-surface it was, however, found that the results for both the general rhombohedron and the rhombic dodecahedron agree fairly closely both as regards the absolute values and the general type of the function with a very simple case, viz., a structure consisting of cubes, four edges of which are parallel to the direction of stress, it being assumed that the cubes are transformed into rectangular prisms. The further assumption, necessary if both phases are liquid, that the volume remains constant, enables us to carry through the complete mathematical treatment.

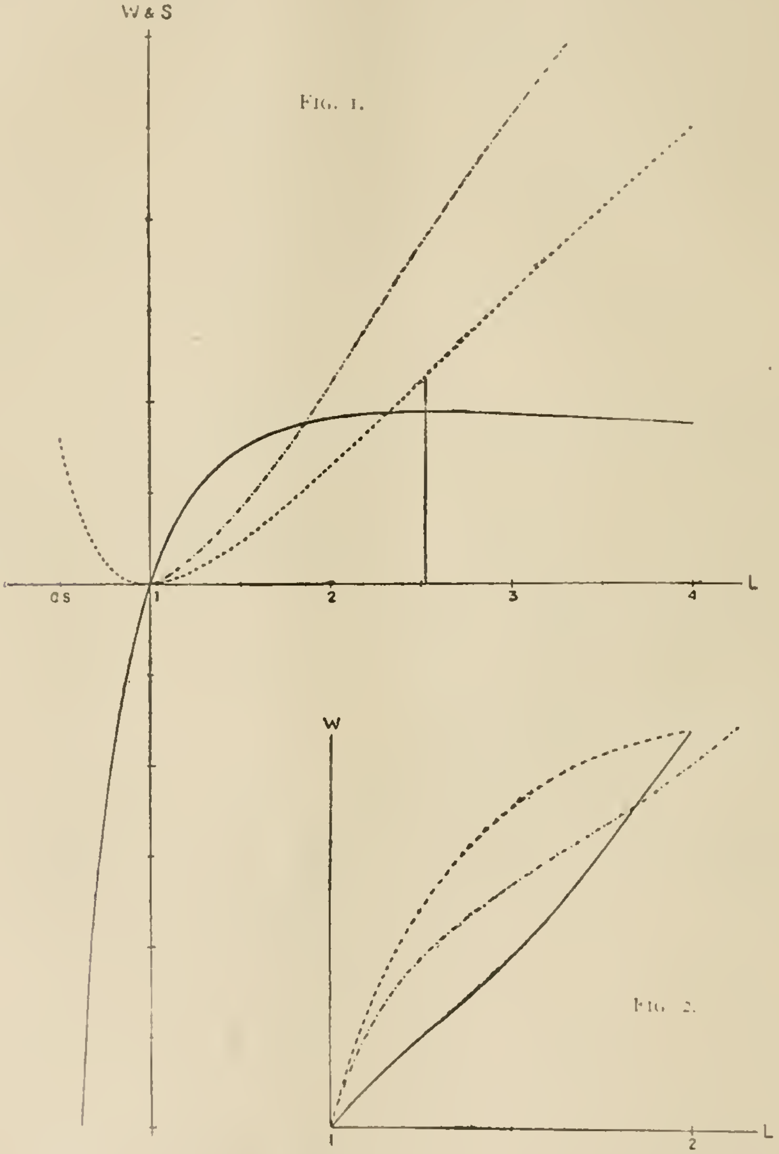

FIG. 1.

FIG. 2.

If we assume a cube with the edge of unit length elongated or compressed to the length L, the section remaining square and the volume constant, the side of the base of the retangular prism so produced will be $\frac{1}{\sqrt{L}}$. The surface of the rectangular prism produced will then be $\frac{2}{L} + 4\sqrt{L}$, and as the original surface of the cube is 6, *the increase of surface* S produced by the elongation or compression L − 1 will be—

$$S = \frac{2}{L} + 4\sqrt{L} - 6 \quad . \quad . \quad . \quad . \quad . \quad 1.$$

This equation is plotted in the dotted curve in Fig. 1 with L as abscissæ and S as ordinates. The curve has an inflexion at $L = \sqrt[3]{16}$; *i.e.*, 2·5198, a point which will be referred to again. (The corresponding curve for cubes stretched along their space diagonal and translormed into rhombohedra is shown for comparison in dot and dash, and the functional identity between the two curves is sufficiently obvious).

The increase of surface produced in stretching to the length L, multiplied by a constant (which expresses the degree of dispersity and the order of magnitude of the interfacial tension) must, as already explained, be equal to the work done in producing that elongation. The work done by the stress W is $\int W dL$, and we have therefore—

$$W dL = K dS, \text{ or } W = K\frac{dS}{dL}.$$

Differentiation of Equation 1 accordingly gives us the equation between the stress and the elongation as follows (for K = 1):—

$$W = \frac{2}{\sqrt{L}} - \frac{2}{L^2} \quad . \quad . \quad . \quad . \quad . \quad 2.$$

The value of W becomes 0 for L = 1, the original length; it is positive and <1 for all values of $L>1$; *i.e.*, for tension, and it is negative and grows rapidly from 0 to $-\infty$ for values of $L<1$; *i.e.*, for compression.

The most striking feature of the function, however, is that the positive arm has a maximum, and, since the ordinates of the W-L curve are the first differentials of those of the S-L curve, it is obvious that the maximum of W must occur for the value of L for which the S-L curve has an inflexion; *i.e.*, for L = 2·5198. The stress-elongation-curve is plotted in full line in Fig. 1., and the occurrence and position of the maximum are clearly shown. The maximum ordinate has the value 0·944.

We thus obtain the very striking result that, if our two assumptions, viz., constancy of volume and the existence of a structure consisting of cubes or rhombic dodecahedra, are correct, *the stress increases until the structure has been stretched to 2·52 times its original length and then slowly decreases.* This result is certainly in direct contradiction with all that is known about the behaviour of elastic bodies, however anomalous it may be in special cases.

It is, of course, impossible to obtain elongations of that order even with dilute gelatin gels, but we can compare experimental stress-elongation curves, as far as they reach, with the theoretical curve. Such curves have been determined by Bjerkens for elongations up to 100 per cent (L = 2), and one set is plotted in Fig. 2 in full line, the theoretical curve being shown to the same scale in dotted line. The failure of the curves to coincide and their marked difference in general character are very striking.

Elongations amounting to many hundred per cent can, however, be obtained with rubber, and for that reason, and on account of the thermal anomalies of the modulus of rubber, there has been a tendency towards postulating a gel structure for rubber. An experimental curve, also due to Bjerkens, is plotted in Fig. 2 in dot and dash. It shows the well-known inflexion at $L \backsim 2$, first observed by Stévart, but differs even more markedly from the theoretical curve than does that for gelatin gel.

Unless, therefore, some structure can be found which is physically possible on one hand, and on the other shows an entirely different behaviour—as regards increase of surface on elongation—from the structures here assumed, the theory that gels consist of two liquid phases must be pronounced untenable. On geometrical grounds it seems excessively unlikely that such a structure could exist, and it is therefore unnecessary to analyse the other difficulties—some of them sufficiently formidable—involved in the assumption of two liquid phases.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

By IRVING LANGMUIR.

(Continued from p. 154).

Adsorption Phenomena at Higher Gas Pressures.—The effect of poisons on the activity of catalysers is essentially the same with gases at atmospheric pressure as at lower pressures. There is every reason for believing that the theory of adsorption outlined in the preceding pages is applicable to the adsorption of gas at atmospheric pressures. In the second part of this paper we shall see that a similar theory also applies to adsorption in surface layers of liquids.

As the pressure of a gas increases the amount adsorbed on a plane surface should gradually increase until the surface becomes completely covered by a layer one molecule (or atom) deep. The surface thus becomes *saturated.* This is in full accord with experimental facts.

In the case of the adsorption of vapours at such high pressures that they approach the state of saturated vapours, there will be a tendency for the adsorbed film to become several molecules deep.

According to this theory it is very improbable that films more than one or two molecules deep would ever be held on a surface by adsorption, except with nearly saturated vapours. We must assume that after a layer two or three molecules deep is formed, the rate of evaporation of additional molecules would be nearly identical with that from the liquefied or solidified gas. If the vapour pressure were well below saturation the rate at which such additional molecules would condense in the surface would be much less than the rate at which they would evaporate. The adsorbed film would thus grow thinner.

There is considerable experimental evidence that the amount of moisture taken up by glass surfaces is greatly in excess of the amount needed to form a layer one molecule deep.

When a 40 watt incandescent lamp bulb is heated to 500° for several hours (after having been exhausted and dried out at room temperature) it gives off about 0·45 cc. of water-vapour, 0·030 cc. of carbon dioxide, and 0·005 cc. of nitrogen (Langmuir, *Trans. Am. Inst. Elec. Eng.*, 1913, xxxii., 1921). The internal surface of this bulb was about 200 sq. cm. The number of molecules of gas given off per sq. cm. was thus 56×10^{15} molecules of H_2O, 37×10^{15} molecules of CO_2, and $0·6 \times 10^{15}$ molecules of N_2. If we calculate the number of molecules of each of the gases necessary to cover a sq. cm. one molecule deep (taking the molecules to be cubical in shape) we find $1·0 \times 10^{15}$ for H_2O, $0·77 \times 10^{15}$ for CO_2, and $0·67 \times 10^{15}$ for N_2. Thus the quantities of gas obtained from this bulb correspond to a layer of water 55 molecules deep, a layer of carbon dioxide 4·8 molecules deep, and a layer of nitrogen 0·9 molecule deep.

The adsorption (?) of water-vapour by pulverised synthetic quartz and anorthite has been studied by J. R. Katz (*Proc. Amsterdam Acad.*, 1912, xv., 445). The amount of water taken up reaches a fairly definite limit when the vapour pressure of the water is about 0·7 of the saturated vapour. The quantities of water adsorbed per sq. cm. of surface under these conditions were $1·3 \times 10^{-6}$ grms. for quartz and $6·2 \times 10^{-6}$ grms. for anorthite. These correspond to layers of water 43 and 205 molecules deep, respectively.

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* From the *Journal of the American Chemical Society*, xxxviii., No. 11.

Freundlich ("Kapilarchemie," Leipzig, 1909, p. 265) reviews the literature on the thickness of adsorbed films, and comes to the conclusion that these films, in general, range from 10^{-7} to 10^{-6} cm. in thickness. Since the diameters of atoms and molecules usually lie between 2×10^{-8} and 5×10^{-8} cm. the adsorbed films, according to Freundlich, should be many molecules thick. The evidence on which this conclusion is based is very meagre, and for the most part is quite indirect. The best data referred to are probably those of Ihmori (*Wied. Ann.*, 1887, xxxi., 1006). According to Freundlich, Ihmori "found with polished metals (brass, steel, &c.) thicknesses for the surface layer of water ranging between 3 and 10×10^{-7} cm., and with quartz an average thickness of 22×10^{-7} cm."

However, by referring to Ihmori's original article it appears that this investigator found that the amount of "adsorbed" moisture increased greatly (about tenfold) if the metal had previously been allowed to stand in the air for a few weeks. With carefully cleaned (polished or ignited) platinum he could not detect any adsorption whatever; that is, the adsorbed film in this case must have been less than 2×10^{-8} cm. thick. Ihmori says "the small amount of water adsorbed by the metals designated as 'polished' is, perhaps, due to the presence of a thin film of oxide."

In Ihmori's experiments the pressure of the water-vapour was about 92 per cent of that at saturation.

From the cases considered above it appears that certain surfaces adsorb moisture in quantities very large compared to that necessary to form a layer one molecule thick. There is no evidence, however, that in any of the cases studied the phenomena is a true adsorption.

The term adsorption should be restricted to gas taken up *on a surface* without any penetration of the gas molecules between the atoms or molecules of the solid surface. The theory of adsorption developed in this paper indicates that the amount thus truly adsorbed should never exceed a layer one or two molecules in thickness.

But there is no reason whatever why molecules of gas or vapour should not penetrate in between atoms of the surface and thus be adsorbed. Dried jellies can absorb large quantities of moisture, and dehydrated salts usually absorb moisture even when no definite hydrates are formed (solid solutions).

The absorption of moisture by a surface of glass is to be looked upon as a process of solution of the water into the glass. Dried sodium silicate absorbs moisture in this way in very large quantities, and it is not at all surprising that this property should not be wholly lost when lime and other oxides are fused with the alkali silicate. The whole behaviour of glass surfaces in giving up their moisture confirms this theory that the moisture penetrates to a very considerable depth into the surface. The remarkable slowness with which the moisture is given up on heating, and the length of time needed for the reabsorption of the moisture, indicates that we are not dealing with a true adsorption phenomena.

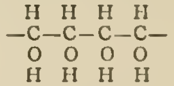
In the case of Katz's experiments with anorthite and quartz there is probably also a penetration of the moisture into the crystal substance. It is, however, quite possible that what he measured was the moisture actually condensed as liquid in the fine capillary spaces between the grains of the extremely fine powder experimented with.

We may safely assume that water-vapour would not penetrate at all into a metal, so that a *clean* metal surface should never take up more moisture than enough to form a layer one molecule deep. This is in accord with Ihmori's results, since he could not detect absorption of moisture by platinum. The other metals used by Ihmori all oxidise in contact with air. The oxide layer formed is usually thick enough to see. When we consider that a film of metallic *tungsten* ten atoms thick only absorbs about 20 per cent of the light striking it, it is evident that a film of *oxide* thick enough to see must be of very great thickness compared to that of a molecule. Furthermore, such a film must be quite porous, since the oxygen required for its growth must have diffused through it. It is therefore not remarkable that relatively large quantities of moisture are absorbed by such films.

Adsorption by Porous Bodies.—Nearly all quantitative measurements of the adsorption of gases by solids have been made with porous bodies such as charcoal. In these cases it is impossible to know definitely the area on which adsorption takes place.

It is often assumed that the surface of even a polished metal is porous to such an extent that its "true surface" is much greater than its apparent surface. As far as the writer knows there is no experimental evidence to support any such assumption, and theoretical considerations would make it seem extremely improbable. The strong surface forces (quite analogous to that in liquids) would tend to make the atoms in the surfaces of solids arrange themselves in such a way as to make the total surface a minimum. Therefore in the absence of definite causes which produce a porous structure (such as those considered below), we should assume that the atoms of the surfaces are packed closely together and are arranged with considerable regularity. Thus a surface of glass should not be considered as porous, although it is capable of absorbing considerable quantities of moisture. The absorption is here a solution process; in other words, a chemical change by which the water molecules become combined (secondary valence) with the atoms of groups of atoms forming the glass. There is no more reason for assuming a porous structure than there is in the case of a liquid.

Truly porous bodies, such as charcoal, probably consist of atoms combined together in branching chains of great complexity. The fibres of cellulose from which charcoal is usually formed probably consist of practically endless groups of atoms—



$$\begin{array}{ccccccccc} & \text{H} & & \text{H} & & \text{H} & & \text{H} & \\ - & \text{C} & - & \text{C} & - & \text{C} & - & \text{C} & - \\ & \text{O} & & \text{O} & & \text{O} & & \text{O} & \\ & \text{H} & & \text{H} & & \text{H} & & \text{H} & \end{array}$$

held together by primary valencies in the direction of their length and by secondary valence in the transverse directions. When the hydrogen and oxygen atoms are driven out by heat the carbon atoms for the most part remain in their chains, but a certain number of cross linkages occur between these chains. The porosity of the charcoal thus undoubtedly extends down to atomic dimensions. The unsaturated state of the remaining carbon atoms explains the practical impossibility of removing the last traces of oxygen and hydrogen from any form of amorphous carbon.

It is evident that with a structure of this kind it is meaningless to talk about the surface on which adsorption can take place. With plane surfaces we have seen that adsorption is usually limited to the formation of a layer one molecule deep, so that we can estimate the maximum adsorption from the extent of the surface. With charcoal, on the other hand, there is no definite surface which can be covered by a layer one molecule deep. Between the atoms of carbon there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, &c. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom. Under these conditions there will be some spaces from which evaporation of adsorbed molecules would occur very slowly, and others from which it would take place much more rapidly. There would be, however, a fairly sharp limit to the number of molecules which could come into intimate contact with carbon atoms. This limit would correspond to the saturated state observable in adsorption even by porous bodies. But it is evident that Equations 14, 15, and 16 which apply to adsorption by plane surfaces could not apply to adsorption by charcoal. The real reason for this failure is that we can no longer assume (as in the derivation of Equation 14) that the rate at which the adsorbed gas evaporates from the surface is proportional to the amount present on the surface.

Strong support for the above views on the structure of porous bodies and the nature of adsorption by them is furnished by experiments in which molybdenum filaments were vaporised in nitrogen at low pressures. These experiments will be described in a future publication. (A brief preliminary description of these results was given in the *Journ. Am. Chem. Soc.*, 1915, xxxvii., 1159).

General Conclusions Regarding Kinetics of Heterogeneous Reactions.

The theory developed in this paper and the experimental work on electron emission and chemical reactions at low pressures leads to the following conclusion :—*In a heterogeneous chemical reaction the activity of a surface depends, in general, upon the nature of, the arrangement of, and spacing of the atoms forming the surface layer.* The atoms forming the second layer below the surface are of importance only in so far as they determine the arrangement of the surface atoms.

In the second part of this paper it will be shown that the surface tension in liquids depends upon these same factors ; in other words, it depends primarily upon the *surface layer of atoms*, and only secondarily upon the group molecules of which these atoms form parts.

According to this view the velocity of reactions in general is not limited by the rate of diffusion through an adsorbed film, but by the rate at which the molecules strike (according to Equation 4) against that portion of the surface which is active. Of course there are many chemical processes which are actually limited by physical factors, such as the rate of diffusion through layers of gas or moderately thick films covering the solids substances. The rusting of iron, the oxidation of aluminium, the solubility of very soluble salts, &c., are examples of this type. But there is no present justification for believing that such physical factors determine the velocity of the typical catalytic reactions.

This theory of heterogeneous reactions can be readily developed along quantitative lines. Some of the principles upon which this development is based have been outlined in a recent paper on the dissociation of hydrogen (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 1145). A brief but more general treatment will, however, not be out of place here.

The velocity of a reaction usually depends on the fraction of the surface which is covered by adsorbed atoms or molecules. This in turn depends on the rate of condensation and on the rate of evaporation of the adsorbed substance. In the sections of this paper dealing with condensation and evaporation we considered only the case where the vapour condensing and the surface on which condensation occurred consisted of the same substance. In the case where different substances are involved, some additional factors must be taken into account.

Condensation.—The surface on which condensation occurs contains a definite number N_0 of elementary spaces per unit area. Let θ be the fraction of these spaces which are unoccupied, and θ_1 be the fraction occupied by adsorbed atoms or molecules.

If each molecule condensing requires only one elementary space the rate of condensation will be equal to $\alpha\theta\mu$ (compare with the derivation of Equation 14). But it may happen that each molecule requires two such spaces before the condensation can occur. The chance that one space will be vacant is θ, but the chance that two given spaces will be simultaneously vacant is θ^2. Therefore the rate of condensation is equal to $\alpha\theta^2\mu$. In general, the rate of condensation will be $\alpha\theta^n\mu$ where n is an integer.

Evaporation.—In evaporation it may occur that two atoms must lie in adjacent positions in order that they may leave the surface together as a molecule. In such cases the rate of evaporation will be $\nu_1\theta_1^2$ instead of $\nu_1\theta_1$.

Chemical reactions may take place either between adjacent atoms on the surface or may occur when gas molecules strike molecules or atoms on the surface. In the former case the velocity of the reaction, in general, will be proportional to $\theta^n\theta_1^m\theta_2^p$ where θ_1 and θ_2 are the fractions of the surface covered by the reacting substances. and n, m, and p are integers. The reason for the occurrence of the factor θ^n in this expression is that the number of elementary spaces occupied by the products of the reaction may be greater than that occupied by the reacting substances. The reaction will thus only occur when vacant spaces are available.

We see that the reaction on surfaces will be governed by a "law of surface action" analogous to the "law of mass action." The velocity in both cases is proportional to a continued product of factors having integral exponents. A radical difference between the two laws exists in the presence of the factor θ^n in the case of reactions on surfaces. (Since $\theta+\theta_1+\theta_2+ \ . \ . \ . \ = 1$ this law bears a close relationship to Reichinstein's "Constant Sum Hypothesis," which has been used to explain various kinds of passivity phenomena).

Let us consider a few simple special cases of heterogeneous reactions.

To simplify the problem we will assume that the velocity of the reaction is slow compared to the rate at which the gas condenses and evaporates from the surface. In other words, we will limit ourselves to a consideration of those cases where the velocity of the reaction is not fast enough to materially affect the equilibrium between the adsorbed film and the surrounding gas.

There are two types of cases to consider. First, those in which the adsorbed film covers only a very small fraction of the surface ($\theta=1$). Secondly, those in which the surface is nearly completely covered by the adsorbed film.

First Case. Surface only Covered to a Small Extent.

Let us consider a single gas which undergoes a chemical change (for example, a dissociation) in contact with a solid body. The rate of condensation on the surface will be $\alpha_1\mu_1$ and the rate of evaporation of the unchanged gas will be $\nu_1\theta_1^n$, where n represents the number of elementary spaces occupied by each molecule of the substance while on the surface. Then, since the adsorbed film is in equilibrium with the surrounding gas, we have—

$$\alpha_1\mu_1=\nu_1\theta_1^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (17).$$

(Note.—This equation becomes identical with Equation 14 only when $n=1$ and $\theta=1$. It is thus seen that the theory of adsorption which led to Equation 16 does not apply to the case where a molecule occupies more than one elementary space. Equation 17 shows that when $n=2$, the amount of gas adsorbed is proportional to the square root of the pressure even at very low pressures. The equations that follow 19, 21, &c., may be derived in several different ways—see *Jour. Am. Chem. Soc.*, 1916, xxxviii., 1149—by making different kinds of assumptions. By experiment it will be possible to determine which set of assumptions correspond with the facts).

Now, the product of the chemical reaction is formed from the adsorbed film by the combination of the substance from m adjacent spaces. In case of a dissociation m will be equal to unity. If ω represents the velocity of the chemical change we have—

$$\omega=\nu_2\theta_1^m \quad . \quad . \quad . \quad . \quad . \quad . \quad (18).$$

Combining these two equations gives—

$$\omega=\nu_2\left(\frac{\alpha_1\mu_1}{\nu_1}\right)^{m/n} \quad . \quad . \quad . \quad . \quad . \quad (19).$$

The velocity of the reaction thus varies with the m/n^{th} power of the pressure (μ) of the gas. In the case of the dissociation of hydrogen molecules by a heated wire we have $m=1$ and $n=2$, so that the velocity at which the gas is dissociated is proportional to the *square root* of the pressure of molecular hydrogen. The recombination of hydrogen atoms in contact with a heated wire, however, takes place in proportion to the *square* of the pressure of the atomic hydrogen. It has been shown previously that these conclusions are in accord with experiments.

Bodenstein and Ohlmer (*Zeit. Phys. Chem.*, 1905, liii., 175) mention that the velocity of the reaction between carbon monoxide and oxygen in presence of heated crystalline quartz is proportional to the pressure of the carbon monoxide and to the *square root* of the pressure of oxygen.

Now, if we assume that each carbon monoxide molecule occupies one elementary space while each oxygen molecule occupies two (*i.e.*, is present on the surface in the form of atoms) we obtain—

$$\begin{aligned} a_1\mu_1 &= \nu_1\theta_1 \\ a_2\mu_2 &= \nu_2\theta_2^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (20), \\ \omega &= \nu_3\theta_1\theta_2 \end{aligned}$$

where the subscript 1 refers to CO, 2 refers to O_2, and 3 refers to CO_2.

These equations give—

$$\omega = k\mu_1\sqrt{\mu_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad (21),$$

where k is a constant involving a_1 a_2, ν_1, &c. Thus the relation found by Bodenstein and Ohlmer follows directly from the assumption that the oxygen adsorbed on the surface is present as separate atoms.

It has been found by Bodenstein and Kranendieck (p. 99, Nernst "Festschrift") that the rate of decomposition of ammonia by heated quartz glass is proportional to the square root of the pressure. It will be shown in a subsequent paper that this fact is readily explainable by assumptions analogous to the above.

Freundlich and Bjercke (*Zeit. Phys. Chem.*, 1916, xci., 1) have recently found that the rate of oxidation of phenylthiourea by oxygen in contact with blood charcoal is proportional to the square root of the concentration of oxygen.

It should be noted that the velocity of gas reactions is frequently proportional to the square root of the pressure, whereas according to the law of mass action we should expect velocities proportional to some integral power of the pressure. The above theory of heterogeneous reactions offers a simple explanation of these fractional exponents. According to the Bodenstein-Fink theory of heterogeneous reactions such square root relations are to be explained by diffusion through films whose thickness varies in proportion to the square root of the pressure. There is definite experimental evidence in the case of the dissociation of hydrogen (which gives a square root relation) that the adsorbed film covers only a very small fraction of the surface with a layer one atom deep. Hence the Bodenstein-Fink theory cannot possibly explain this case. It is very probable that such square root relations are never caused by diffusion through adsorbed films.

(To be continued).

WAR SERVICE OF CHEMISTS.

The following circular has been sent to the members of the American Chemical Society:—

In accordance with the resolutions passed by the Society at the Kansas City meeting the officers of your Society have been urging the government that chemists, as in England, Canada, and France, be used for chemical service in the war, either in the employ of the military branch, of the other government branches, or of necessary industries. A special committee was organised by your President, consisting of Dr. W. H. Nichols, Chairman, Drs. M. T. Bogert, A. A. Noyes, your Secretary, and your President, to lay definite recommendations before the authorities. These have been published in the July number of the *Journal of Industrial and Engineering Chemistry*.

The government, it appears, has decided that there will be no general exemption of any class of men as a class—for reasons which are eminently wise and necessary at the present moment. At the same time, no doubt, it is anxious to see every man used in what appears to it to be the right place for him. It has seemed perhaps best to make no general ruling whatsoever, except to the effect that there will be no class exemptions, and to leave all individual cases to the federal district exemption boards, to which exemptions for industrial, agricultural, and professional reasons are left by law.

Under the circumstances, in the absence of instructions from the government and in view of the general desire on the part of our members for guidance and advice in this matter, we would recommend to you *unofficially* the following procedure: Chemists of military age selected by draft for service and accepted by the local boards to which the physical examination, &c., is committed are advised to submit to their federal district boards:

1. An official certificate of their employers, or of the university or college from which they have received degrees or with which they have been or are connected, certifying as to their education and experience as chemists.
2. An official statement by their employers of the nature of their work as chemists.
3. A recommendation, if such seems right, from their employers, or their university or college, that they be assigned to continue their work as chemists.
4. A request that in default of such assignment, they be detailed to serve as chemists in the military branch of the government.
5. If enlisted in any capacity, inform the Secretary of the Society by postal card of the company, regiment, and corps in which you are enrolled, in order that a record may be kept of the fact and the War Department advised from time to time of chemists in the Army should their services as chemists be required.

The purpose of this recommendation is to put into the possession of the government authorities all the facts necessary for it to decide exactly for what service a given man is most fitted. We believe this to be in accordance with the resolutions adopted at the Kansas City meeting and in accordance with the patriotic duty of every American chemist to serve his country under the selective draft in the capacity the government itself, with a full knowledge of the circumstances, selects for each individual.

Julius Stieglitz, President.
Charles L. Parsons, Secretary.

Washington, D.C., July 24, 1917.

ALLIED TRADING PUBLICATIONS, LTD.

The recent creation by the British Government of the Belgian Trade Committee shows that the time has come to examine the means to favour the development of trade between Great Britain and her Allies.

The Allied Trading Publications, Ltd., has been established with the definite object of making known the industrial and commercial resources of Great Britain to each of the countries brought into close relation with her through the war.

The capital for embarking on this enterprise has been subscribed by disinterested people who have been attracted by the general interest of the subject. On the other hand, the promoters of the Allied Trading Publications, Ltd., have found in the members of their committee of patronage the moral support derived from such well known names in British economic science as Sir George Askwith, K.C.B., K.C., and Sir Thomas Elliott, Bart., K.C.B., and the distinguished chairmen of the French and Belgian Chambers of Commerce in London.

A book is at present in course of preparation in which all the resources of Great Britain will be detailed. This volume, besides an introduction referring to different questions of commercial and industrial interest, will contain a series of articles written by specialists showing the essential details of each branch of industry. After each article pages will be at the disposal of traders to display their specialities.

The work will be published simultaneously in French, Russian, and Italian, and will be distributed *gratuitously* in Belgium, France, Italy, and Russia through the medium of Chambers of Commerce, federations, and industrial associations, so that it will be in the right hands at the right moment. As a matter of fact, Belgium, the North of France, and Russia will save precious time if, when their territory is liberated, their contractors, manufacturers, and merchants are able to correspond direct with British firms to whom they will necessarily have to apply for their requirements. With regard to Italy, the rupture of her commercial relations with the Central Empires makes it imperative that she should at once learn the resources at her disposal.

It is essential that no room shall be left for the commerce of Germany, which will, beyond all doubt, try to insinuate itself into the very countries she has ruined.

The special advantage of this publication is that each manufucturer, trader, or producer who desires his name mentioned in connection with the special articles on his branch of industry is assured of a circulation of at least 10,000 copies in each country, that is 40,000 copies, with the special recommendation that they will be given away free of charge by suitable organisations to those they will interest.

Victoria House, 117, Victoria Street, London, S.W. 1.

ACETIC ACID.

Extending the Order of the Minister of Munitions of September 21, 1917, as to Acetic Acid.

Whereas by an Order dated September 21, 1917, the Minister of Munitions, in pursuance of the powers conferred upon him by Regulation 30 A of the Defence of the Realm Regulations, applied that regulation to certain war material, namely, glacial acetic acid and acetic acid of a purity of 60 per cent and over; and whereas the Minister of Munitions is desirous of applying that regulation to acetic acid of all strengths; now, therefore, the Minister of Munitions hereby orders that on and after the date hereof the war material to which that regulation applies shall include, in addition to the war material specified in the said Order of September 21, 1917, the following war material, that is to say, acetic acid of all strengths.

(All applications and enquiries regarding this Order should be addressed to the Director, Chemical Section, Trench Warfare Supply Department, St. Ermin's Hotel, Westminster, S.W. 1).

NOTICES OF BOOKS.

The Public School System in Relation to the Coming Conflict for National Supremacy. By V. Seymour Bryant, M.A. London, New York, Bombay, Calcutta, and Madras: Longmans, Green, and Co. 1917. Pp. xviii+78. Price 1s. 6d. net.

We are possibly becoming too much accustomed to being confronted with articles and books on the defects of the public school system to pay the heed to them which the subject undoubtedly deserves, but it is to be hoped that those who can state the arguments in favour of changes with vigour and temperance will not desist until some very definite reforms have been made. This book contains a moderate statement of the indictments which may be made against the present average curriculum. The evils of early specialisation are shown, and the general characteristics of the public school curriculum are analysed before the *rôle* of science in the educational scheme is discussed. Some very telling examples of the wastefulness of scientific ignorance on the part of the authorities are included, and suggestions are made as to the syllabus of the general scientific work which should be covered by every boy at the preparatory or public school. The book contains a preface by Lord Rayleigh, and also a reprint of the essentials of a liberal education as outlined in the Essays of Huxley.

Proceedings of the National Academy of Sciences of the United States of America. Vol. III., No. 6, June, 1917. Baltimore: Williams and Wilkins Company. Price 0·50 dols.

The aim of this journal is the publication of brief accounts of the work of American investigators in all branches of science, so as to secure the prompt spread in other countries of a knowledge of discoveries. Full details and long tables of data are omitted, but the articles are more than mere summaries of results, for in every case accounts are given of the methods employed and sufficient data to warrant the conclusions drawn. This aim is well fulfilled, and the journal has a very real value for scientific men. In this number the articles deal with a wide range of subjects, some of the titles of those on physics being the "Stark Effect in Helium and Neon," the "Triplet Series of Radium," the "Occurrence of Harmonics in the Infra-red Absorption Spectra of Diatomic Gases," while the other branches of science treated include geochemistry, genetics, and agriculture.

Combinazioni Chimiche fra Metalli. ("Chemical Combinations between Metals"). By Dott. Michell Giua and Dott. Clara Giua-Lollini. Milan: Ulrico Hoepli. 1917. Pp. xvi.+446. Price L.12.50.

This book gives a very concise account of the compounds of metals among themselves, and it certainly fills a gap in Italian, if not international, scientific literature. Larger and more detailed works on the same subject are obtainable, but this has the special merit of presenting its information in the most convenient form for reference. Diagrams and methods of thermic analysis are first briefly described, and a chapter on the physical properties of the intermetallic compounds follows and gives a very complete *résumé* of the subject. Then brief descriptions are given of all known intermediate compounds with references to the sources from which the information has been obtained, and these are finally tabulated with a complete bibliography and well indexed.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxv., No. 3, July 16, 1917.

Study of the System Water, Uranyl Oxylate, Sodium Oxalate.—A. Colani.—The solubility curves of this system reveal the existence of the previously unknown compounds $Na_2(UO_2)_4(C_2O_4)_5.11H_2O$ and $Na_2(UO_2)_2(C_2O_4)_3.5H_2O$. The author has also obtained a pentahydrate of $Na_2(UO_2)(C_2O_4)_2$, but has not been able to prepare Wyrouboff's salt, $Na_6(UO_2)_2(C_2O_4)_5.13H_2O$.

Alcohols and Bases of Vacuum Tar.—Amé Pictet, O. Kaiser, and A. Labouchère.—In vacuum tar there are small quantities of oxygenated compounds of alcoholic function and nitrogenous compounds with basic properties. By treatment with dilute hydrochloric acid the bases can be extracted and the alcohols may be isolated by boiling the liquid with sodium; hydrogen is evolved and a deposit of solid alcoholates is formed. Five alcohols and six bases were thus separated. The lowest alcohol was *p*-methylcyclohexanol, and the others which were not identified belonged to the hydroaromatic series. The lowest base corresponded to the formula C_7H_9N, and appeared to consist of a mixture of toluidines. The other derivatives were secondary unsaturated bases. Apparently the alcohols of vacuum tar exist as such in the coal.

No. 4, July 23, 1917.

This number contains no chemical matter.

No. 5, July 30, 1917.

Carburation of Iron by Alkaline Cyanides and Cyanates.—M. Portevin.—Mixtures of varying proportions of potassium cyanide and cyanate with iron were heated, and the degree of carburation of the iron was determined. It was thus found that at temperatures from 750—900° the addition of a certain amount of cyanate considerably increases the carburating power of potassium cyanide.

Action of Metaphosphoric Acid on Molybdenum Oxides.—A. Colani.—The author has already shown that metaphosphoric acid at a red heat acts upon UO_3, giving uranous metaphosphate, $2P_2O_5.UO_2$, with loss of oxygen, and the same derivative is obtained by the action of the acid upon UO_2. At a red heat metaphosphoric acid causes a slight reduction with MoO_3, with evolution of oxygen, while MoO_2 is split into a lower oxide, Mo_2O_3, which gives a metaphosphate, and a higher oxide, which remains dissolved in the acid.

No. 6, August 6, 1917.

Refractory Properties of Silica.—H. Le Chatelier and B. Bogitch.—When a brick made from refractory clay is crushed at 1500° it flattens and the edges become rounded, while with a silica brick the same pressure produced at first no appreciable effect. When the pressure was increased, however, the silica brick finally broke, the broken pieces resembling in shape those normally obtained on breaking hard materials by compression. Good silica bricks contain from 3 to 5 per cent of basic oxides, and the weight of sulphates obtained by the action of hydrofluoric acid and sulphuric acid varies from 8 to 14 per cent.

New Case of Reversible Catalysis; Direct Formation of Nitriles from Amines of the same Carbon Chain.—Paul Sabatier and G. Gaudion.—When vapour of benzylamine is passed at 300—350° over reduced nickel benzoic nitrile is formed. But at this temperature the hydrogen liberated reacts on the amine to give toluene and ammonia, the reaction being—

$$3C_6H_5.CH_2.NH_2 = C_6H_5CN + 2C_6H_5NH_2 + 2NH_3.$$

One-third of the amine is thus transformed into benzoic nitrile. A similar reaction occurs with iso-amylamine, isobutyl cyanide being obtained. When copper is used as catalyst instead of nickel the products obtained are much more complex.

Bulletin de la Société Chimique de France.

Vol. xxi.-xxii., No. 6, 1917.

Cyclisations with Elimination of a Nitro Group.—S. Reich and B. Turkus.—When an alkali is added to an alcoholic solution of the hydrazones of 2.6 dinitrobenzoic aldehyde a rapid change of colour occurs, the solution turning from red to blue and finally bocoming pale yellow. On addition of water 1-phenyl-7-nitroisoindazol is precipitated. If one of the nitro groups in the original compound is replaced by chlorine or bromine the same cyclisation occurs, the sole difference being that the reaction takes place only at the temperature of the water-bath, while in the preceding case it occurs in the cold. The cyclisation occurs with the phenyl hydrazone of the aldehyde, but not with that of 2.4-dinitrobenzaldehyde, probably because in the 2.6-derivative there is a great accumulation of atoms in the neighbhoorhood of the CH group, which increases the instability of the molecule.

MISCELLANEOUS.

Literary Intelligence.—Lord Rhondda will contribute an introduction to the new edition of Sir William Crookes's book on "The Wheat Problem," which Messrs. Longmans will shortly publish. An additional chapter on Future Wheat Supplies has been contributed to the book by Sir R. Henry Rew, K.C.B.

Coprolites.—A correspondent, interested in the production of wheat, asks for information on the value of coprolites as a phosphatic fertiliser, and would be glad to be put in touch with an expert who would tell him. He also is desirous of obtaining information regarding the geological formation these minerals are likely to be found in, the probable depth from the surface, the chemical constituents of the same, the percentage of fertilising matter they are likely to contain, and their present unit value. Any information as to the process for converting the raw material into a commercial manure would also be of great value.

The Electro-positive and Negative Ions of Dichromic Acid.—The value of the second chromic acid radical, CrO_3, in the molecule of dichromic acid, as determined by the following experiments to quantitatively determine it, is in favour of the two CrO_3 groups not being structurally equivalent, as might be expected, and is considered the cause of the ready solubility of strontium chromate in CrO_3 excess when slightly alkaline. That the precipitation of the chromate follows electro-chemically as to the + and − nature of the ions is also considered evident, in that with molecular equivalent quantities of strontium chloride and nitrate, the ratio of precipitation of the chromate with potassium hydrate as the neutralising agent is 9·5 to 3·6, with NaOH 4·8 for the chloride, and with sodium carbonate 7·5 to 5 for the chloride and nitrate.—J. C. Thomlinson, B Sc., 15, Denmark Street, Gateshead-on-Tyne.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Anhydrous Ammonia.—I shall be greatly obliged for the names and addresses of firms who can supply anhydrous ammonia (99·99 per cent pure (not aqua ammonia).—K. J. Tarachand.

NITROGENOUS COMPOUNDS FROM METALLIC CARBIDES.

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THE CHEMICAL NEWS

VOL. CXVI., No. 3020.

CHINA'S NEED OF SCIENCE.

By FRANK BROWNE, F.I.C.,
Formerly Government Analyst, Hongkong.

THE time is opportune for drawing attention to China's need of science for the expansion of her trade and the development of mineral industries. Already for commercial purposes the aid of the analyst has proved valuable in several ways. By the examination before shipment, the quality and the freedom from adulteration of some important native products have been ensured. Business has thus been made easier for the Chinese producer, the Chinese middleman, and the exporter. This system has given satisfaction to all concerned in Hongkong, but it is necessary that it should be extended now to other ports. Tous at Hankow, there is an enormous export of tung or wood oil, and the introduction of the Hongkong method of sampling and subjection to certain specified physical and chemical tests would be an easy matter and would prove very beneficial, particularly in saving losses due to shipments of interior material. Experience has shown that, when once adopted for valuing one article of export, analysis has soon been applied to others.

It has been reported that a national analytical bureau has been operating for some years in Japan and has proved very successful.

In China this kind of work cannot be left to the private individual, even if one could be found willing to undertake it. The analyst carrying out the test needs a fixed salary, and such a position that buyers and sellers alike may look upon him as a referee, with no particular person's interest to consider. An analyst attached to the service of the Municipal Council of the Port would prove an acceptable arrangement, or probably one under the direction of the British Government would be found to suit the merchants of all nationalities just as well, and the officer might be obtainable more easily. At most places the fees charged would cover the cost of the upkeep of the testing station. Even if this were not balanced the facilitation and augmentation of trade would be such as to convert the question of expense into a matter of quite secondary importance.

For the examination of native products the best and most rapid analytical methods are necessary. The goods come into port, and it is to everyone's advantage to have them certificated, sold, and shipped off as speedily as possible. It might be mentioned here that it is desirable for an analyst who has accepted an Eastern appointment to acquire early a knowledge of procedure in his correspondence with various European officials. This is practically the same as used in Government departments in England, and is easily learnt.

Another pressing need for scientific help is in the development of the mineral wealth of China. As is well known the superstitution of *fung-shui*, in which there is a rooted objection to disturbing the surface of the soil, has done much to retard China's progress. However, there are now a number of enlightened native officials who would gladly see the country opened up. Caution is necessary, as the people are easily upset by any interference connected with their ancestor worship. But in order to value a mining property, and to recommend a suitable method for obtaining the mineral or metal, there is no doubt that in many cases a good deal of excavation might be needed. The Chinese do not want usually a very elaborate opinion. They would like, in the case of a mineral such as stibnite or molybdenite, an opinion on the spot as to what is the substance, the value delivered at one of the ports, and any recommendation as to the best means of freeing from earthy impurities. The Chinese official would probably say that he was willing to devote so many dollars to the matter, so as to start working on a very small scale. The time has not come yet for a mining expert in China to be able to have sufficient consulting work to pay his expenses. And yet there is no doubt that were the services of such available the exploitation of the country would proceed much more quickly. In years to come the Chinese will have their own experts, but at present they place much more reliance on the opinions of Europeans. Two mining engineers stationed at Hongkong would find their services in request in various portions of South China. Especially at first there would be periods in which there would be little to do, but this would not matter very much, as their training could be utilised in carrying out work in one of the several scientific laboratories in Hongkong. Ability to speak Chinese would be of much assistance to them. One of the dialects, such as Cantonese, might be studied first. After a time this knowledge would serve as a useful check on interpretation. To be able to speak with natives when travelling in districts where Europeans are few and far apart would always be useful.

Attention has been drawn to two particulars in which science could assist China's commercial expansion. Western help is needed in these, as trained native workers are too few, and in most cases too inexperienced. China's need of science in directions other than those indicated is obvious to those knowing her industries, but sufficient for the present will have been done if to the point treated there be given some practical consideration.

THE

MANUFACTURE OF NITRATE OF AMMONIA BY ELECTRIC POWER AT COKE-OVEN PLANTS.*

By E. KILBURN SCOTT, A.M.I.C.E., M.I.E.E.

OWING to the scarcity of sulphuric acid, nitre cake has been tried for mixing with acid to make sulphate of ammonia, but it is hardly suitable, because of the considerable admixture of sodium sulphate, and the author proposes to show that makers of coke can easily turn their ammonia by-product into nitrate by means of acid of their own manufacture; also that by making their own acid they become entirely independent of the acid associations, which have for so long controlled supplies in this country.

The nitric acid required for nitrate of ammonia may be very dilute—of, say, 25 per cent to 33 per cent strength—and it is easily and cheaply made from the air by electric power. The process is not new, because nitric acid has been made from air on a very large scale for many years in Norway, Italy, and France. Further, one of the most striking scientific developments of the war has been the way in which Germany, by fixation of atmospheric nitrogen, has become entirely independent of Chili nitrate and of sulphuric acid.

Atmospheric nitrogen may be fixed in two ways:—First, as ammonia, and secondly, as nitric acid. In order to fully appreciate these methods it will be useful to set out in tabulated form the various ways of making these two compounds.

Ammonia can be made—

(*a*) As a by-product in the manufacture of coke in regenerative and in waste heat ovens.

(*b*) As a by-product in the manufacture of lighting and heating gas for town supply.

(*c*) As a by-product in the Mond process for production of power gas from slack coal.

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* A paper read before the Coke Oven Managers' Association (Midland Section), July 28, 1917. From the *Colliery Guardian*, August 3, 1917.

(*d*) As a by-product in the application of the Mond process to the production of power gas from peat.

(*e*) As a by-product in connection with distillation of bastard and lignite coals.

(*f*) As a direct product by acting on superheated steam on calcium cyanamide, which latter compound is obtained by combining pure nitrogen with calcium carbide.

(*g*) As the direct product of the synthetic combination of pure nitrogen and of pure hydrogen in the presence of a catalyst, by the process due to Prof. Haber.

When ammonia is obtained as a by-product of the distillation of coal, the cost may be, as in the case of most by-products, only a little above the interest charge on the recovery plant plus the cost of operating same. It certainly is not correct to arrive at the cost of by-product ammonia by deducting the value from the market price of sulphate of ammonia. About £30 a ton or 3¼d. per pound is quite high enough to take for the ammonia, but the proposal to make nitrate of ammonia at coke ovens would still be a good commercial proposition, if the ammonia was at a higher figure.

As a comparison it is of interest to determine the cost of ammonia made from calcium cyanamide. As the cyanamide and the carbide from which it is made require electric energy, clearly the rate for electric power is a factor. We may assume ⅛d. per unit, which for 8000 hours a year is a little over £4 a kw. year, and at this rate the cost of the cyanamide may be taken at £10 per ton. To produce one ton of ammonia requires about 4½ tons of cyanamide, containing 18 per cent of nitrogen, and therefore the cyanamide will cost £45. In addition there are certain other manufacturing costs, but to cut it short we will take a total of £50 a ton, or about 5¼d. a pound.

It would be interesting to know the cost of synthetic ammonia as made by Haber's method from pure nitrogen and pure hydrogen; but although we can arrive at the costs of the two gases, the other data are not available, because the process is only in use in Germany.

Nitric acid can be made in any of the following ways—

(*a*) The action of sulphuric acid on sodium nitrate or Chili saltpetre. This method is practically universal in this country.

(*b*) Fixation of atmospheric nitrogen by the direct process using electric arc flames. This method is employed on a very large scale in Norway, and is in use in Italy, France, Switzerland, Germany, and Austria. A factory is to be built in Manchester.

(*c*) Oxidisation of ammonia in the presence of a catalyst by the process due to Prof. Ostwald. This method is employed on a large scale in Germany, and is also in use in Italy, France, and Belgium. A small plant has been built at Dagenham Dock, in Essex.

When discussing the cost of nitric acid, one method is to assume it is of 100 per cent purity, although in practice, of course, there is no such pure acid, and for the manufacture of most compounds quite low percentage strengths will do.

When made from Chili saltpetre costing, say, £10 a ton, which was approximately the price before the war, the cost of pure acid may be taken at £20 a ton, or say about 2·15d. a pound. The price of Chili nitrate is now nearer £25 a ton, and as the cost of sulphuric acid, labour, &c., has also gone up, the present cost of nitric acid must be upwards of £50 a ton.

In order to compare the cost of nitric acid as made by the direct arc-flame process, the author has taken the cost of electric energy at ⅛d. per unit, or about £4 a kw.-year of 8000 hours. Assuming a yield of 200 grms. of 33 per cent acid per kilowatt-year, which is equivalent to 66 grms. of pure acid, the calculated cost of pure acid is about £13 10s. a ton, or 1·44d. per pound.

The oxidisation of ammonia into nitric acid depends on the cost of the ammonia, and if we take it at £50 per ton, as above mentioned, the cost reckoned as pure acid should be about £25 a ton. It is very doubtful, however, if it can be made at this figure, owing to the lack of experience of the process and the very high cost of the catalyst —platinum, which has to be replenished from time to time.

We have now to consider the various methods for making the ammonia and the nitric acid into nitrate of ammonia, which are briefly as follows:—

1. By direct mixing of strong ammonia with strong nitric acid made from nitrate of soda. This method is employed by Chance and Hunt.

2. By the reaction of sulphate of ammonia with calcium nitrate, or nitrate of soda. This method is employed by Brunner, Mond, and Co

These are pure chemical methods, whereas the two following depend on the use of catalysts

3. By the combination of ammonia made from calcium cyanamide, with nitric acid made from the ammonia by a catalyst. This method is employed in France and Germany, and a factory has been built at Dagenham Dock, Essex.

4. By combination of ammonia made by the synthetic or Haber process, with nitric acid made by oxidation of ammonia by a catalyst. This method is employed on a large scale in Germany.

There is finally the purely electrical method with which the paper is mainly concerned, viz.:

5. By direct mixing of ammonia solution with dilute nitric acid of about 25 per cent strength, made from air by the direct arc-flame process.

Power from Coke Ovens.

The scheme proposed is that gas from regenerative coke ovens, or the steam raised by waste-heat ovens, should be utilised in an electric power house, built by the coke oven proprietor, and some, if not all, the energy be employed for making nitric acid from air—this acid to be then combined with ammonia from the ovens to make nitrate of ammonia. In other words, the idea is that coke-oven proprietors should manufacture nitrate with *home-made* nitric acid, instead of, as at present, making sulphate with *purchased* sulphuric acid.

Power may be obtained by using the surplus gas from regenerative ovens in gas engines.

A battery of 50 regenerative ovens of, say, medium size Coppée type, will coke 360 tons of coal per day. Taking coal of average quality, containing 10,000 cu. ft. of gas per ton, and assuming 50 per cent as being surplus gas, there would be 1,800,000 cu. ft. of surplus gas per day. Large gas engines working on such gas have been found to use about 21 cu. ft. per break-horse power per hour, so this quantity of surplus gas should develop:

$$\frac{1,800,000}{21 \times 24} = \text{about 3500 horse-power}$$

which, with modern electric generators is equivalent to about 2500 kw.

Power may also be obtained from waste heat ovens by using the steam in high-pressure steam turbines.

A battery of 50 waste heat ovens of, say, medium size Coppée type, will furnish enough waste heat to raise about 350 tons of steam per day in high-pressure boilers. If the steam is superheated, and used in modern steam turbines, a consumption of about 11 lb. of steam per horse-power per hour is attainable, and the power should therefore be—

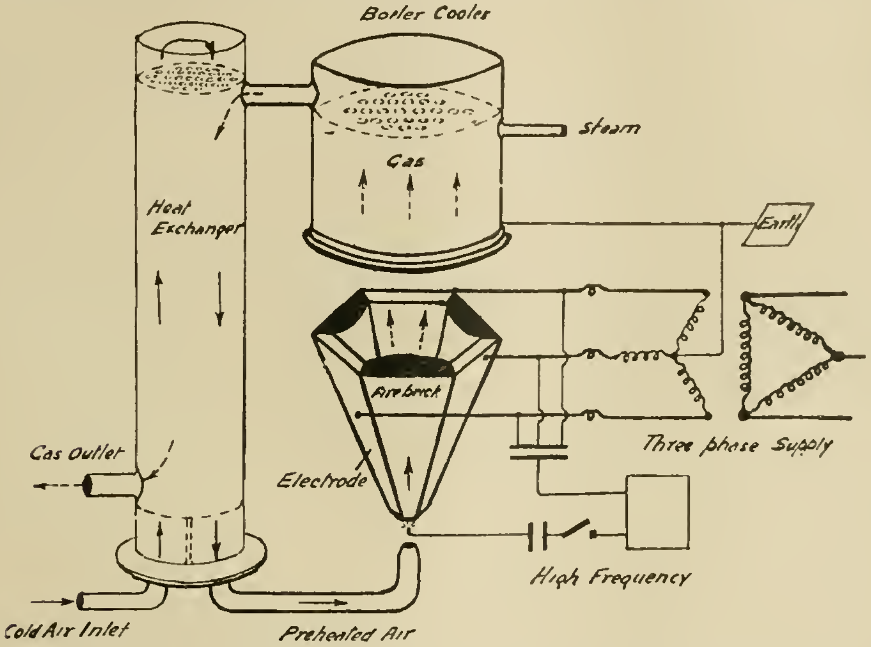
$$\frac{350 \times 2240}{11 \times 24} = \text{about 3000 horse-power}$$

which, with modern electric generators, is equivalent to about 2000 kw.

According to Sir Wm. Garforth, much gas from coke ovens goes to waste, but whether that is so or not, it is clear that as modern coke ovens take the place of the old beehive type a great deal of power will be available. The same authority has said—

The time has now arrived when coal should no longer be regarded simply as a fuel. Of the quantity carbonised, 5,000,000 tons a year were burned in "beehive" ovens without obtaining the recovery of by-products. This quantity alone represented a loss to the nation of 70,000 tons of ammonium sulphate, 250,000 tons of tar, and 12,000,000 to 15,000,000 gallons of benzol, all of which could be saved if the coal were distilled in retort ovens.

Cost of Power House.—When making estimates it is convenient to take round figures whenever possible, so that the main points at issue may be quickly appreciated, and adjustments easily made to suit other conditions. Therefore, although it has been shown that a battery of 50 coke ovens will give 2000 kw. to 2500 kw., the author proposes to give figures for a plant capable of generating 1000 kw. and also for an electro-chemical factory to utilise that amount of energy. Readers must remember, however, that the larger the plant the lower the first cost per kw. installed.



Sketch Diagram of Kilburn Scott Three-phase Furnace.

For a total of 1000 kw. the best size of generating unit to adopt is 500 kw., and it is advisable to have three such units, one of them being spare.

The following is the approximate cost of power-house plant for utilising coke oven gas in direct coupled gas engines:—

Three 500 kw. vertical type gas engines direct coupled to three-phase alternators complete with two motor-driven circulating water pumps for the engine jackets, compressed air starting equipment, also piping and valves; gas mains from ovens to purifiers and thence to gas engines, also the purifiers to rid gas of sulphur before passing it to the gas engines: cost £28,000.

The following is approximate cost of power-house plant for utilising waste heat to raise steam for turbines:—

Three 500 kw. steam turbo-alternators of Westinghouse or other good type, each complete with condenser, motor-driven extraction pump, valves, and fittings, £20,000; also steam-raising equipment for above, consisting of boilers and superheaters, economiser, steel chimney, feed pump, steam and water piping, also gas mains from ovens to boilers, £9000; total, £29,000.

It will be seen that for the size of power-house the price is about the same for each kind of plant. For larger sizes the cost of a steam plant is lower than a gas engine plant, also the limiting size of a gas engine unit is about 1000 kw. Steam turbine units can be built for practically any output, and the larger they are the better they work, and the lower the steam consumption.

Gas engines give high thermal efficiency, but unless precautions are taken they do not work well with coke-oven gas, because of the snappy action due to high-percentage hydrogen.

Electric power-houses are now so standardised and the installation and running of same is so simple and straightforward that coke-oven proprietors need not hesitate to instal their own plant. The author is sure they would find it more profitable to utilise the surplus gas or heat to make nitrate, &c., than to sell the gas, &c., for others to exploit.

Leaving a fair margin of profit, electric energy ought to be supplied from such a power-house at ½d. per unit. At this figure 1000 kw. for 8000 hours a year would bring a return of—

$$\frac{1000 \times 8000}{8 \times 240} = £4166.$$

From this must be deducted the standing charges, labour and stores, and also any figure that the coke-oven proprietor feels justified in fixing for the gas or waste heat. As he is selling to himself it is merely a matter of book-keeping.

Electro-Chemical Factory.

The plant required to fix atmospheric nitrogen as nitric acid consists of:—Electric furnaces and boilers; switch gear and instruments; fans for air supply and circulation of gases; apparatus for cooling and oxidation of the gases, &c. Also the acid and alkali absorption towers or chambers, complete with acid elevators or *montejus* and distributors, &c.; reservoirs and mixing tanks; evaporators, crystallising and drying plant, &c.

Furnaces.—The furnace described herein is that which the author has specially developed for the purpose. It differs from those in use abroad in that it is a self-contained three-phase unit, and as such it has various advantages.

All the furnaces used abroad are of the single-phase type, and, therefore, on a three-phase supply they have to be run in sets of three. There are certain disadvantages in working single phase, and a rough-and-ready analogy is to compare a single-phase and three-phase furnace to engines having a single crank and three cranks. All electric motors are wound for three-phase because they are so much more efficient and better in every way than single-phase motors. So it is with electric furnaces.

This furnace has three triangular metal electrodes arranged with intervening refractory material so that together an inverted conical space having six sides is formed. Air passes into this conical space, and when the furnace is working, the arcs which are struck between the electrodes where they are near together at the bottom are extended into flames by the flow of air.

The flames start and stop with each alternation of each phase, and there are thus always three flames working together, so that, to the naked eye, the cone is completely filled. The three currents of the three phases react together and rotate very rapidly, the speed of rotation being governed by the frequency of supply, which is usually 50 periods per second.

As the particles of air pass upwards they come in contact with the rapidly rotating triple arc flames, and the nitrogen and oxygen are caused to combine to form nitric oxide, or to employ an expression often used, "the nitrogen of the air is fixed."

The rotating triple arc flames of a three-phase furnace are a great advantage over the single flames of a single phase furnace, because all the air is enabled to come into contact with the flames. The single arc of a single-phase furnace can only exist in one plane, as it were, and consequently a great deal of air passes through such furnaces without coming in contact with the air arc.

The nitric oxide which is formed when air comes in contact with an electric arc has to be chilled rapidly, and for the purpose there must be a cooling zone in close proximity to the arc flame. Natural movement of the air removes the gas from the hot part of the flame, but a boiler is also used as the roof of the furnace to hasten the cooling. This is very effective by reason of the latent heat of steam.

Where the generating plant has a mixed-pressure steam turbine, steam from those boilers can be be utilised in the turbine and the combination worked regeneratively. By so doing there is a gain of over 10 per cent.

After passing through the boiler the gases flow through a heat exchanger and part of the heat is transferred to the air entering the furnace. It has been found advantageous to use as high a degress of preheat as possible—namely, over 250° C.

By working the three arcs together in this way, it is possible to maintain a very high temperature, because the energy varies between 0·86 anb 1·0. With three separate flames in three separate furnaces the energy in each must pass between 0 and 1·0 twice in each period.

There are greater radiation losses with three separate furnaces because of greater wall area, and requiring double the number of electrodes.

By combining three arc flames together, a balance load is obtained automatically, because current is always flowing in one or other of the phases, thus enabling the arcs to maintain each other. This is good for the supply and regulation of power.

A feature of the furnace is the use of high frequency pilot sparks in the space between the electrodes where they are close together. These break down the air dielectric, and the electrodes can be placed at the best distance apart for the passage of air.

The recognised method of measuring the yield of a furnace is to find the output of dilute nitric acid which it gives in a given time for a given amount of electric energy. The acid is resolved into the equivalent amount of pure nitric acid of 100 per cent strength, and the electric energy input to the furnace is measured in Board of Trade units, or kilowatt-hours.

Usual yields for single phase furnaces are about 50 grms. per kilowatt-hour with 60 as a maximum. Careful tests carried out over a considerable period with the author's three phase furnace have shown considerably higher yields.

Nitrate Plant.—The nitric oxide is transformed into nitrogen peroxide on cooling, and this in turn is converted into nitric acid in an absorption plant of some usual type. The resulting dilute acid is run into a closed iron tank containing ammonia solution in which the ammonia is at about 25 per cent strength. Acid is slowly added to a large volume of liquor, and an agitator mixes them together, the heat of combination being carried off by cooling coils as well as by circulation of air.

The addition of acid continues until nearly all the ammonia is taken up, leaving a slightly alkaline reaction.

The ammonium nitrate solution is then run through a filter into vacuum pans, where evaporation is effected by steam coils at a pressure of 20 mm. of mercury.

When nearly all the water has been evaporated the solution passes into long troughs slighly inclined and subjected to a rocking motion. The nitrate forms into small crystals with no enclosure of liquor, and after the crystals have been dried in a hydro-extractor they are placed in bags or barrels ready for market. The nitrate is absolutely pure.

It has been mentioned above that the ammonia was brought up to 25 per cent strength, and that concentration is absolutely necessary in order to reduce the water when the solution has to be carried any distance. Nitrate of ammonia can, however, be made with solution of much lesser strength; in fact, it has been demonstrated at Bristol that nitrate can be made direct from ordinary gas-works liquor by acting on it with dilute nitric acid. Of course when made in this way the nitrate is not so pure as when made with concentrated ammonia and a great deal of evaporating plant is necessary.

(To be continued).

CAN THE HUMAN SPECIES BE IMPROVED?

By SAMPSON MORGAN.

Authorities Quoted.—Zeno, Diogenes Laërtius, James Martineau, Mivart, Huxley, Herbert Spencer, Carlyle, James Beattie Crozier, Haeckel, Shelley, Froude, Lecky, Moncure Conway, Walt Whitman.

TELL me the name of the genius who first said, "All the actions of man are decided by his relation to things," and I will tell you the name of the greatest teacher who has ever arisen among men. The clean culture axiom that man is what his food makes him, is simply another form of the same truth. Diogenes Laërtius wrote that Zeno of Citium, the founder of the Stoical School, was the first who said the chief good was confessedly to live according to nature, but the claim is not convincing. The Stoics also held that the world is an organic whole, and that the unity of the world involves the sympathy of all its parts. They also popularised what I call the grandest truth in the world, which has permeated the writings of most of the ablest thinkers through the ages to the present time.

James Martineau said, "You understand a particular kind of animated being when looking inwards you see how its parts constitute a system, and, again, looking outwards and around, how this system stands with regard to other types of organised existence."

Mivart said, "We comprehend anything better the more we know of other things distinct from but related to it." The writings of Darwin, Huxley, Herbert Spencer, and equally eminent investigators, also show how remarkably the Stoical teachings had influenced their conclusions, Nevertheless, though these scientists recognised, with Mivart, that man's body can only be comprehended by means of an extensive acquaintance with the bodies of other animals, they failed to see that man is linked up as much with the inorganic, mineral, and vegetable as with the animal kingdom. "The world is an organic whole."

Still, although the Stoics devoted much attention to logic and treated as a tenet the proposition that "All the actions of man are decided by his relation to things," they insisted that everything in the world existed for the benefit of some other thing. "Plants exist for the support of animals, and animals for the support of man." Strange both Huxley and Herbert Spencer held similar views. But they arise, in my opinion, from a thoughtless exclusion of logic and physical truth; that is, of truth pertaining to physics perceptible to the senses, since through both we see in the clearest manner possible that we being phytophagous not carnivorous animals the food of the latter cannot form the food of the former.

The opinion I challenge is due to the non-recognition of the fact that food is the essence of the contract for life between nature and man, and that this contract cannot be treated as a scrap of paper with impunity. The belief that animals exist for the support of man was held millions of years before the advent of the Stoical School, for it was the crude faith of the River Drift men of the Miocene period.

For forty years I have sought to discover the secret of physical, mental, and moral perfection, and I am satisfied that I have succeeded. Unlike all other investigators who have started from the highest rung of the ladder of life, I have started from the lowest rung—the dust—to which fact, together with persistent experimentation, I mainly attribute my success.

The proper study of mankind is matter. That is the teaching of nature. It is true that my propositions in the main are in direct disagreement with the opinions of philosophers and physicians, but many of these men are, to my mind, influenced too much by tradition and imagination.

The problem of health and harmony remains unsolved by the nations. The demons of disease and war are more active and relentless than ever. The losses sustained through the action of both are appalling. "I swear," says Walt Whitman, "there can be no theory of any account unless it corroborates the theory of the earth." Clean culture corroborates that theory in the most comprehensive manner.

Haeckel says, "An entirely new character has been given to the whole of our modern civilisation, among other things, by our astounding theoretical progress in sound knowledge of nature," and adds, "On the other hand, we have made little or no progress in moral and social life in comparison with earlier centuries."

No matter what authority we consult the same complaint confronts us. All are dissatisfied, perplexed, and troubled at the superficiality of the advancement made, and the cause of this complaint is, I hold, the lack of that sound knowledge of nature which Haeckel so erroneously boasts we have acquired.

In respect to the controlling factor in advancement, James Beattie Crozier says that though the Church and Carlyle agreed it is procured by preaching duty and morality, the view taken by Herbert Spencer and the State, that this progress is best maintained by improvement in material and social conditions, is the truest philosophy. He states, "In this world things make their own relations, that is to say, their own morality, in spite of politicans and priests." But I suggest that it is made for them, is inherent in the universe, for morality consists in strict conformity to the laws of nature which are the laws of life.

Moral Food from Moral Soil.

Lecky wrote, "The greatest of all results to be expected in any field are to be looked for in the study of the relations between our physical and our moral natures." I claim that clean culture is that study. With regard to our physical natures doctors have accomplished practically nothing. The most thoughtful and learned members of the profession tell us plainly that humanity all the world over is on the brink of a huge collapse. It is even seriously estimated that diseases are increasing so rapidly as to endanger the existence of the race, and at the present rate of increase in less than 200 years there will not be enough healthy people in the world to care for the ailing members of the human family.

Froude says, "We must go into the council chamber of nature." I have been there and return with the truth, that perfection depends upon the consumption of moral food from moral soil.

My long-continued experiments and observations show in the most convincing manner the unity of the animal with the mineral, and in a way that has not hitherto been acknowledged. They demonstrate beyond question the remarkable similarity of the nature of the ailments which affect the animal and vegetable kingdoms, the treatment and the remedies requisite for a cure in each case being almost alike. This is an emphatic verification of the theory of the unity and oneness of all things. With the persistent increase in the multitudinous list of diseases which affect the animal kingdom there is a corresponding increase in the diseases which affect the vegetable kingdom also. The coincidence is too remarkable to ignore.

The eating of weak tissued foodstuffs by men, and the feeding of imperfect plant foods to soils, is the primal cause of the trouble. Thus food stands forth as one of the greatest factors in health and progress.

Moncure Conway wrote, "Poisons or allied substances imported into the system often have the power to make the victim over into their own image; not only the outer body and expression may be changed, but the nerves, temper, and instincts have their reins held in strange hands, while the conscious will of the driven man sits helplessly by."

Who, then, can doubt the tremendous influence of food, or question the possibility of man, dieted upon excessive quantities of inflammatory flesh, becoming as savage and inhuman as the wild beasts of the jungle.

Pavy says, "In vegetable products we find not only the organic but likewise the inorganic matter we require, and, in taking up and applying mineral matter as it does to its own purposes of growth, as well as for forming organic compounds, the vegetable organism contributes in a complete manner towards the supply of what it wanted for animal nutrition."

For its true and natural food the vegetable feeder has to go to the vegetable kingdom direct. Here, then, we have the order of nature in respect to foods and feeding.

The plant possesses the faculty of producing and building up organic substances from the air and soil. Hence it is a constructive. The animal has no such faculty. It must look to the plant for organic substance, which it breaks down and digests. Hence it is a destructive. In the first sub-class of mammals the first order comprises the Primates; that is, man and the apes. In this order, as regards man, there are two separate sections, one established by nature—vegetable feeders; the other by custom—flesh feeders.

The plant furnishes the perfect pabulum for the former direct, the latter gets its pabulum second-hand, through flesh in an imperfect form. The plant—the constructive—alone produces the perfect food for the vegetable feeding animal—the destructive; and in face of this order of nature it is immoral for one plant destructive animal to feed upon the flesh of another plant destructive animal. How, then, can the consumption of animal products by man be justified?

In respect to the economic aspect a brief consideration will show that, whereas one acre under spade culture will produce food for one man living on vegetable products, ten acres will be needed to feed him on meat; so that for every ten acres used for stock, nine acres are wasted. Whereas under arable one man can find constant occupation on five acres, under permanent pasture only one man is wanted for fifty acres. Under this system the loss through the curtailed production of foodstuffs, added to that through the displacement of labour, is as wanton as it is wicked.

The True Source of Evil.

The great teachers of India and China, among others, ever insisted upon the importance of pure thought; but the benefits of pure thought, which most intelligent beings will readily admit is of transcendent consequence, cannot possibly be enjoyed except through the medium of pure food. The one without the other is inconceivable.

Herbert Spencer's opinion from the biological point of view was, that we must regard as good the conduct which favours self-perservation, and as bad the conduct tending to self-destruction. So he insisted, that along with the increasing power of maintaining individual life, which evolution brings, there goes increasing power of perpetuating the species by fostering progeny, and that in this direction evolution reaches its limit when the needful number of young, preserved to maturity, are then fit for a life that is complete in fulness and duration.

The ideal moral man, he says, is one in whom the moving equilibrium is perfect, or approaches nearest to perfection. Each function has some relation, direct or indirect, to the ends of life. It is immoral to treat the body so as in any way to diminish the fulness or vigour of its vitality. Hence results one test of actions. Does the action tend to mainteoance of complete life for the time being, and does it tend to prolongation of life to its full extent?

The responsibility of each individual is thus brought home by Herbert Spencer in the most direct and emphatic manner possible. Flesh eating, then, whether Herbert Spencer intended his argument to prove it or not, becomes, from his own propositions, an immoral action, because it reacts injuriously upon the human structure, bringing in its train derangement and deterioration.

By manipulation the juicy, sugary, and oily fruits may readily be made to furnish the most perfect nutrients for mental or manual workers, as well as for young or old. Grains are essential for their phosphates and other minerals. Literary and sedentary workers in the cities suffer in considerable numbers from various forms of ailment, which in many cases are apparently incurable. Yet there is hardly a case that cannot be alleviated if not cured by the aid of a frugal properly balanced non flesh dietary.

Plethoric conditions are fatal to health and fruitfulness. In refutation of the claims of those who insist upon the necessity of a high nitrogen percentage for full crops I would mention the fact that in 1837 a grain of oats having accidentally fallen on a quantity of burnt clay in a field belonging to a Mr. Juckes, of Cockinge, produced 19 stems and the astonishing number of 2345 grains.

In 1915 I planted a medium sized potato in a mass of bonfire ash which had been placed in a heap on garden soil, and in the autumn when dug up the plant had 36 good sized potatoes hanging to its roots.

In 1916 I bought of a cottager a gallon—8 pounds—of potatoes at the end of May which had come from Romney Marshes. Each potato was as shrivelled, flat, and dry as an evaporated Normandy pippin. I planted them in the first week in June in poor soil, to which nothing had been added. When in the trench I poured a gallon of water on each seed, and earthed them all up. In the autumn I dug 84 pounds of splendid potatoes from them. When bought the seed cost me fourpence.

Where did all these wonderful plants obtain the necessary nitrogen to mature such crops if not mainly from the air?

But what is the moral food, and what is the moral soil, upon which I place such value?

The moral food consists mainly of the sun-ripened and sun-dried fruits, together under certain conditions with grains and some green products. I term them moral foods because they are the true natural and perfect foods for man, coming as they do from the vegetable kingdom direct.

The moral soil is a clean sweet soil in which there is no filth material such as dead or waste animal matter whatever. It is a soil practically in which only the good nitrifying organisms thrive, and being fed with uncontaminated waste vegetable matter, through green manuring preferably, and dust of the primary or felspar rocks, with a perfect conveyer of lime in a bland form, induces fertility, which may be maintained indefinitely without any other form of plant food being furnished to it. This assures the elaboration of that healthy internal tissue in roots, fruits, and grains which alone furnishes the human organism with everything that is vital for the maintenance of perfect health and strength of body and mind.

Yet with these truths confronting us a writer recently said, "Nature seems wholly non-moral and quite callous as to suffering. She seems to bestow as much care in developing the lung tubercle as she does in tinting the crimson spot on the consumptive's face. She seems as patiently purposive in developing cancer as she is in preparing the mechanism of the vocal chords, which shall thrill thousands with a very heaven of joy, in a great soprano's voice. She is as painstaking in evolving evil as she is in developing good. She is callously non-moral.

But in these very words the writer himself, though he does not see it, shows by the glaring contradiction they contain, that he fails to distinguish between nature's virtue and man's vice.

The whole of my investigations prove conclusively that it is man who is non-moral and callous to suffering. That he, and he alone, is the cause of the lung tubercle and the crimson spot of consumption, besides being the originator and perpetuator of cancer and of evil. It is man and not nature who is callously non-moral.

In the face of the facts I have set forth, the perverse influence in man, the existence of which has so completely mystified moralists, philosophers, and theologians, is now for the first time proved to be due to his diet. Imperfect food produces imperfect natures, imperfect natures produce imperfect brains, imperfect brains produce imperfect thoughts, and imperfect thoughts produce imperfect actions. It cannot be otherwise. Thus the perverse influence denounced as evil is due to unnatural food.

The Stoics, unable to explain the problem of the existence of physical evil, put forward the subtle proposition that imperfection in details is necessary for the perfection of the whole. With regard to moral evil they were undoubtedly nonplussed, and though they paid much attention to the relation of outward circumstances to morality they failed to consider, as I have done, the relation of inward circumstances to morality, not only in respect to the internal composition and influence of animal tissue, but to the internal composition and influence of vegetable tissue, by which, for the first time in the history of health and morals, the transcendent power of that hitherto unperceived factor—the food of the food—is made clear.

Unduly stimulate the animal propensities by inflammatory diet, and the perverse influence is stirred into resistless activity. Derange the physical stamina and the moral equilibrium is disturbed, and disease follows. In each instance the results are due to the undeviating workings of natural law. Clean culture thus deals with moral pathology on truly scientific lines and offers perfection to man—through food.

Rapid Determination of Manganese and Chromium in Metallurgical Products.—M. Travers.—Manganese and chromium can be determined in steels by adding nitric acid and ammonium persulphate in presence of silver nitrate, which acts as a catalyst, and then titrating with sodium arsenite. The method is applicable to chrome steels and is very rapid.—*Comptes Rendus*, clxv., No. 5.

THE METALLURGY OF THE RARER METALS.*

By J. W. RICHARDS.

(Concluded from p. 165).

Boron.

As an intermediate element, semi-metal, cheap and abundant in its compounds, yet almost unknown as an element, boron is very interesting. Although quoted at several dollars per oz., yet there are possibilities of it being made for *x* cents per lb., where *x* may be anything over 25. It is only the prophetic prescience of the enthusiastic metallurgist, however, that can discern the goal in the distant future.

Boron occurs in nature as its oxide, Sassolite, containing 31 per cent of boron, as borax, containing 11·5 per cent of boron, and as colemanite, containing 18·9 per cent of the metal. These sources are comparatively abundant, the oxide being found in volcanic districts, borax near dried up lakes, and colemanite (calcium borate), being literally a waste product of the borax mining, for which uses have only recently been developed.

Gay-Lussac and Thenard, Wöhler and Sainte-Claire Deville reduced the oxide by potassium or sodium, other chemists by phosphorus, magnesium, aluminium, and calcium, while Duncan reduced boron chloride gas by hydrogen. Chemically, its reduction does not appear to be of extraordinary difficulty. Electrochemically, Davy electrolysed fused boracic acid, Gore potassium borofluoride, and Faraday fused borax. All describe having isolated boron. Quite recently, Weintraub has decomposed boron chloride by hydrogen in a high-tension arc, and obtained purer boron and in larger quantity than any previous investigator. His classical paper is in the *Transactions of the American Electrochemical Society*, 1909, xvi., 165.

The properties of the pure boron obtained by Dr. Weintraub are exceedingly interesting. Its fusing point is extremely high, between 2000 and 2500° C.; it was fused in a boron nitride crucible under the pressure of its own vapour. Its boiling point is near to its fusing point; it has considerable vapour tension as low as 1600° C. It has a conchoidal fracture, and is nearly as hard as the diamond. At room temperature it is electrically almost a non-conductor, but at 500° C. its conductivity has increased 2,000,000 times; at 1000° C. its conductivity is of the order of that of the metals. Applying moderate voltages to a cold piece, it soon warms up and makes itself a good conductor. Such extraordinary properties suggest its use for many interesting electrical contrivances, which are enumerated by Dr. Weintraub.

Other uses of boron, which have not yet been thoroughly investigated, are in the formation of boron steels and boronised copper. The former were investigated by Guillet, in France, with irregular results; in some respects, at times, the effects were similar to that of vanadium in the famous vanadium steels, at other times the results were different. The uncertainty may have been due to irregular composition of the ferro-boron alloy used. A great amount of investigation should be done on this line, first in making a reliable quality of ferro-boron, and second in using it systematically in various qualities of steel. The question of boronised copper is in a still greater state of uncertainty. Boron or even boron suboxide (B_7O, or perhaps boron saturated with B_2O_3), added to melted copper enables a perfect copper casting to be obtained of practically 100 per cent electrical conductivity; a trade product sold as boronised copper has similar effects in producing sound copper castings. These results are only the beginning of an extensive field of investigation of the effects of small amounts of boron on metals and metallic alloys. They will certainly lead to important metallurgical discoveries and improvements.

In metals and alloys boron can act chemically, as a purifying or refining agent to remove oxygen, nitrogen, and perhaps sulphur, phosphorus, and dissolved oxides, while in larger amount it acts metallurgically as an alloying element. In the latter respect it forms true alloys, such as the ferro-boron alloy, which is an article of commerce. The possibilities of extensive use in molten metals and alloys are great, but mainly dependent upon systematic metallurgical research in properly equipped laboratories.

The production of the metal and its alloys also needs expert attention. For use in steel a good uniform quality of ferro-boron is needed, and the manufacture of this in satisfactory uniform quality has not yet been mastered. Some years ago the Pacific Coast Borax Company offered a prize of 500 dols. to be awarded by the American Electrochemical Society, for a practical electric furnace method of producing ferro-boron directly from calcium borate (colemanite), a waste product of the borax mines. A few years later the prize money was returned by the Society to the Company as not having been earned, although several attempts were made for it. For use in copper, brass, and bronze, cupro-boron alloy answers as well as having pure boron. One method of making this is being tried, and the product is giving some very satisfactory results. Improved and more certain means of getting boron into copper are needed, and could probably be found by a moderate amount of careful investigation. As for pure boron and the fascinating possibilities dependent on its remarkable properties Dr. Weintraub's method makes the product, but at considerable expense, and a cheaper easier method is a great *desideratum*. If such is found, boron will certainly occupy an important place among the useful metals

Chromium.

This element is also common and abundant in nature, and rare and expensive as a metal. Chromite, containing 34 per cent of chromium, costs normally 20 to 25 dols. per ton, while the ferro-chromium alloy produced from it sells at 100 to 550 dols. per ton, according to the percentage of chromium and carbon contained. But pure chromium, carbon-free, is produced only by reduction of chromium oxide by aluminium, and commands 75 cents per lb. The use of chromium in steel is rapidly extending to all varieties of extra hard and high-speed steel, but the use of pure chromium is limited by the high cost of its production and our lack of knowledge of how to handle it and its possible useful effects. For example, chromium electro-plating is white and durable, and for many purposes may be superior to nickel, and almost equal to platinum plating, but the technique of always getting perfect plating has not been satisfactorily mastered. Cobalt-chromium alloys have been made which have some of the remarkable properties and uses of high-speed tool steel (stellite alloy of Mr. Haines). This is an excellent example of totally unexpected and valuable physical properties being discovered by systematic investigation. These alloys, however, must be made from pure chromium and not from ferro-alloy. How many other remarkable alloys yet remain to be discovered by patient and intelligent investigation no one knows or can even guess.

As for the methods of reduction, ferro-chromium alloy carrying high carbon (6 to 8 per cent) is produced quite cheaply in crucibles, cupola furnaces, blast furnaces, or electric furnaces. Low carbon ferro-chromium commands three to five times as high a price, because of the difficulty of decarbonising the raw product. It is very much to be hoped that tests will be made in the electric shaft-furnace to see if it is not possible to produce directly from the ore a low-carbon product. The thing has been done in the case of pig-iron, producing a low-carbon product which is called pig-steel; there is no inherent impossibility in similarly mastering the conditions for producing directly the low carbon ferro-chromium. The present prices of the two products, 100 and 500 dols. per ton, respectively, would warrant great efforts in that direction.

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* Presented at the 8th Semi-Annual Meeting of the American Institute of Chemical Engineers, Cleveland, June 14, 1916 From the *Journal of Industrial and Engineering Chemistry*, viii., No 8

Similarly, chromium is not a difficult metal to reduce to the metallic state, but it is a difficult question to find the proper flux and to keep carbon out of it. Goldschmidt reduces it by aluminium; electrolysis of its fused salts is difficult because of their high melting-points. If electrolysis of aqueous solutions of chromium salts could be satisfactorily controlled so as to produce heavy deposits, this might open the door at once to cheap and pure chromium. Electrolysis of molten relatively fixed salts in which chromium oxides are dissolved (similar to the Hall aluminium bath) is not a hopeless proposition. The chromium would be plated solid, however, on chromium cathodes, since the working temperature would be below the melting-point of chromium.

The metallurgy of chromium is full of attractive possibilities, and the usefulness of pure chromium in the field of alloys is only beginning to be scratched; the scratching, however, is proving very much "worth while."

Titanium.

Our friend Mr. A. J. Rossi and the Titanium Alloy Manufacturing Company, of Niagara Falls, are the alpha and omega of the titanium industry. Nearly fifteen years ago my first introduction to Mr. Rossi was in the historic barn at Niagara, the cradle of so many of the Niagara Falls industries. Mr. Rossi was running the electric furnace and Mrs. Rossi was in the little laboratory making the necessary analyses.

Everyone knows of the enormous masses of titanic iron ore in northern New York and Canada, which contains so much iron and so little sulphur and phosphorus, that every blast furnace would be glad to get it if it was not for the titanic oxide which makes it so unworkable that you could not give it them. Mr. Rossi tried first to extract the iron only, throwing away the titanium in the slag; but this was not profitable. He then turned to producing ferrotitanium alloy for use in steel and cast-iron, and by indomitable perseverance has made that a success. A finely written booklet of over 100 pages, published by his company and to be had for the asking, tells the whole story, so why take up time to rehearse it here? Get the booklet and read it. In addition to titanium treatment of steel, to deoxidise and denitrogenise, this company also makes a specialty of titanium-treated aluminium bronze, also of titanium-treated bronzes and brasses of various compositions.

With titanic iron ore carrying 10 to 15 per cent of titanium as cheap as iron ore, and if iron-free material is required, rutile, 60 per cent titanium, at 5 to 7 c. per lb., there is no lack of cheap raw material. If uses are found for pure titanium, however, some other than the electric furnace must be used to reduce it, because, in absence of iron, titanium carbide would result. The methods for producing pure titanium are, like its prospective uses, still in the future, but they nevertheless are worth study and work. One can buy titanium metal now at about the price of silver, but if the problem were properly faced it could probably be made as cheaply as chromium.

Molybdenum.

Molybdenum sulphide, MoS_2, 60 per cent molybdenum, looks almost exactly like graphite, and is about as widely distributed. Normally, it can be purchased as 90 per cent concentrates at 25 c. per lb. This would make the raw material for 1 lb. of molybdenum cost nearly 50 c.; the selling price of the metal is about 2·00 dols. This leaves a large margin to pay for reduction. In fact, 1·00 dol. per lb. of contained molybdenum ought to return the reduction works a good profit.

However, the principal need of the molybdenum industry is a better utilisation of its sources of raw material. The deposits have not been, in general, properly prospected or opened up, and then not properly worked. They are usually low-grade propositions, with 5 to 10 per cent of molybdenite disseminated through hard rock. This calls for careful study of crushing and concentrating methods, so as to minimise waste and loss. In most cases the actual treatment falls far short of this, and possibly half the molybdenite in the ore is lost. The producers of the concentrates are being paid high prices for their material, but the market is limited and dull. If molybdenite were sold cheaper, there is little doubt that ferromolybdenum, 50 to 85 per cent molybdenum, could be sold at half its present price, and the uses of molybdenum in steel correspondingly increased. New uses have also been found, such as the molybdenum wire so useful in electric resistance furnaces. This wire is scientifically very useful in that it resists the alloying action of many liquid metals even at very high temperatures. Dr. C. G. Fink, of the Edison Lamp Works, has studied these notable physical and chemical properties, and has described them in the *Transactions of the American Electrochemical Society*, 17 (1910), 229.

Zirconium.

We may mention this element, which, as metal, is rare enough, but whose oxide has recently been found in considerable abundance. The familiar mineral Zircon is the silicate, containing nearly 50 per cent of zirconium, but it is found only in limited amount. In the last ten years the oxide Baddeleyite has been found in large quantities in Minas Geraes, Brazil, running 75 to 95 per cent pure, giving 50 to 75 per cent of the metal. This source is now so common that it sells at 4 to 5 c. per lb., and is being used in large quantities as a refractory material, on account of its high melting point (2000° C.), high resistance to all kinds of slags, low thermal conductivity, and low coefficient of expansion.

The metal, however, is almost an unknown quantity. It has been obtained by the action of potassium or sodium on the anhydrous fluorides. Fused, it is white, density 6·4, melting point 1500° C., hard enough to scratch quartz. Ferro-zirconium has been made in the electric furnace, and used in small amounts in steel, with rather indefinite results. And yet, if some very useful properties of zirconium were discovered, the metal could undoubtedly be prepared at a reasonable price—only a fraction of the 5·00 dols. per oz. now asked for it as a chemical curiosity. How it is to be obtained cheaply is one more of the interesting questions confronting the metallurgical pioneer.

Cerium.

There is a peculiar interest attaching to this metal and its close associates, from the fact that hundreds of tons of fairly rich cerium material is lying on the waste heaps of the incandescent mantle factories. The thorium ore used by these factories is monazite—a phosphate of the cerium earths plus thorium silicate. On extracting the thoria the residue is worthless for mantle fabrication. It is known as "Commercial Cerium Carbonate," and contains cerium, lanthanum, neodymium, praseodymium, samarium, gadolinium, yttrium, ytterbium, a little thorium, and considerable alkalis, iron, phosphoric acid, and silica. By treatment with acids precipitation of the rare earths, and ignition, a chocolate-brown mixture of oxides of the rare earths is obtained, in which cerium oxide predominates, and which contains nearly 50 per cent of metallic cerium. When this mixture is reduced directly, without further separation, to the metallic state, an alloy of the rare earth metals is obtained which is known as mixed metal (Mischmetal), or impure or commercial cerium. The composition of mischmetal naturally varies, but may be taken as approximately 30 to 50 per cent of cerium, 15 to 25 per cent of lanthanum, 10 to 15 per cent of the didymiums, up to 20 per cent of the yttrium metals, and 1 to 5 per cent of thorium.

An immense amount of laboratory and practical work has been expended on the production of mixed metal and of purer cerium. Professor Muthmann and his students in Munich, and Alcan Hirsch in the United States, deserve particular mention for their articles in *Liebig's Annalen* (1902 to 1910), and *Transactions of American Electro-*

chemical Society, 1911, xx., 1—102, respectively. Dr. Auer von Welsbach was the pioneer in the commercial manufacture and use of mischmetal. Annoyed by the sight of heaps of the cerium residue around his mantle factories, he experimented with their reduction to mischmetal and with the possible uses of the latter. Finding that it gave off sparks when scratched, he conceived the idea of using it in automatic lighters, but found that it sparked far too feebly and unreliably to be practical. He then thought that if he purified the cerium it might give sparks more freely, but on making the purest cerium he found it to spark less than the impure metal. Turning in the opposite direction, he took mischmetal and added to it alloying metals not of the rare earth class, and found that they increased the sparking property. Iron, for instance, when increased to 30 per cent gave an alloy with remarkable spark-giving properties, such as make it most efficient and reliable in automatic lighters. This has formed the basis of the "pyrophoric alloy" industry, since, although other metals have similar effects, the 30 per cent iron alloy is probably the best sparking alloy, for general use, so far made.

The electrolysis of fused cerium salts, double chlorides or double fluorides, to give the melted mixed metal is carried on on a large scale in Austria at Treibach, in Germany near Berlin, and was commenced in the United States, in 1916, near New York City, by Mr. Hirsch and his associates The technique is not easy to master, and all the works keep their operations as secret as possible. The principal difficulties are the re-solution of deposited metal, metal fog, and scattering of the metal as fine globules or "metal-mush" through the electrolyte, making it difficult to unite the metal to one melted mass. Since the latter trouble is largely due to surface tension, a study of this property, particularly how it can be diminished, might help in overcoming the difficulty. As an example of the opposite effect, the cupelling of lead on a bone-ash muffle depends absolutely for its success on the surface tension of the molten lead. But metallic tellurium in quite small percentage *decreases* the surface tension of the lead so greatly that the metal *wets* the cupel and cupellation is rendered impossible. Arsenic, on the other hand, *increases* the surface tension of melted lead, and is therefore purposely added, about 0·25 per cent, to lead being made into lead shot, in order to make rounder shot. A physical study of such effects on cerium might well assist in overcoming the scattering of the metal in globules in the electrolytes. Another direction in which improvement might be made would be the careful study of the eutectics of mixtures of cerium salts with barium salts, so as to find an electrolyte of lower melting point in which the losses by re-solution of deposited metal would be less than they are at present. Another possible improvement would be the finding of an electrolyte which would dissolve cerium oxide or the mixed oxides directly, and give metal by electrolysis. Such a bath has been discovered for aluminium oxide, and a long experimental search for a similar bath for the cerium oxides would be amply justified.

The possibility of using the 30 per cent iron alloy as a melted cathode, and enriching it in cerium by electrolysis, might be considered. If we had the fusing point curve of cerium-iron alloys we could draw some useful conclusions in this direction. The addition of small amounts of other metals to the bath, so as to produce other useful cerium alloys directly, might facilitate the electrolytic operation. Further experience with the process, particularly by those familiar with the electrolysis of molten baths for sodium, magnesium, or aluminium, will very probably lead to considerable improvements and reductions of cost.

The uses of cerium and particularly of its alloys are sure to increase, and may attain considerable proportions. It has been proposed by Borchers as an addition in small quantity to aluminium, to improve its properties. But the large use will always be the pyrophoric alloys, which have so largely replaced matches. Before the European war over 3000 workers were employed in Austria in this industry of pyrophoric alloys and automatic lighters. Mistakes were made in the early days of the industry, and some alloys put into lighters which crumbled to pieces by the time the apparatus reached Australia, but continual improvement was being made, until a satisfactory substitute for matches was attained. The improvement most needed in the pocket lighting apparatus is to be able to dispense with alcohol or similar liquid; a wick impregnated with a *solid* combustible which can be ignited by a pyrophoric alloy would give a great impetus to this art.

The author apologises for making this paper so largely critical and prophetic. If it has sounded too prospective in tone, the excuse must be that it is inherent in the subject. Some of these elements are among the most common in nature, yet they remain so rare in practical life that they are still chemical curiosities. But the chemical curiosities of one age have frequently become the chemical commonplaces of the next age, and even within a generation some of us have seen this happen under our own eyes. Let us, then, be foresighted, forehanded, and anticipate possible developments a little by such a general review as has just been given, so that when some wonderful changes and improvements are made in the next few years we may have the satisfaction of knowing that we glimpsed their shadows some time before they arrived, and may even have assisted in hastening their arrival.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART I.—SOLIDS.

By IRVING LANGMUIR.

(Concluded from p. 172).

Second Case. Surface nearly Completely Covered.

LET us consider a reaction in which two gases are in contact with a solid body. One of the gases, which we shall designate by the subscript 1, is present in such quantity and evaporates so slowly from the surface that the surface remains nearly completely covered by an adsorbed film of this substance. A second gas, 2, undergoes a chemical change when its molecules come in contact with the uncovered surface. This reaction may be of several kinds. For instance, the gas molecules condensing in vacant spaces may dissociate, may react with the underlying solid, or may react with the adsorbed gas in adjacent spaces. The rate at which the first gas will condense is $a_1\theta^n\mu_1$, where n is the number of elementary spaces occupied by each molecule which condenses. The rate of evaporation will be constant ν_1, since the surface is nearly covered. Therefore for equilibrium—

$$a_1\theta^n\mu_1=\nu_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (22).$$

The rate at which the second gas will enter into reaction will usually be proportional to $\theta\mu$. It is quite possible, however, in some cases that θ may have any integral or even fractional exponent. We thus obtain for the rate of reaction—

$$\omega=\nu_2\theta\mu_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (23).$$

Combining these equations we find—

$$\omega=\nu_2\theta_2\left(\frac{\nu_1}{a_1\mu_1}\right)^{1/n} \quad . \quad . \quad . \quad . \quad . \quad (24).$$

The velocity of the reaction is thus proportional to the pressure of gas 2, and *inversely proportional to the n^{th} root* of the pressure of gas 1.

Now this is a relation which has been found to hold for a very great number of heterogeneous reactions in which the velocity is influenced by catalytic poisons. A few of these will be briefly mentioned.

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* From the *Journal of the American Chemical Society*, xxxviii., No. 11.

Fink ("Dissertation," Leipzig, 1907; see also Bodenstein and Fink, *Zeit. Phys. Chem.*, 1907, lx., 1) found in the case of the reaction (in contact with platinum) $2SO_2 + O_2 = 2SO_3$ that the velocity is proportional to the pressure of SO_2, and inversely proportional to the square root of the pressure of SO_3. This relation follows directly from Equation 24 if we place $n = 2$. We may thus conclude that the platinum surface was practically completely covered by a layer of adsorbed SO_3 in which each molecule of SO_3 required two elementary spaces for its condensation. Fink actually measured the amount of adsorbed SO_3, and found it to be of the order of magnitude of a single layer of molecules. According to the Fink-Bodenstein theory the amount of adsorbed SO_3 in these experiments should have been proportional to the square root of the SO_3 pressure, whereas according to the above theory the amount adsorbed should have been practically independent of the pressure (saturation). It is, however, obvious that a film one molecule thick (as found by Fink) cannot have a *thickness* which varies in proportion to the square root of the pressures over a wide range.

Bodenstein and Ohlmer found that the reaction between oxygen and carbon monoxide in contact with quartz glass takes place at a rate proportional to the pressure of oxygen, and inversely proportional to the pressure of carbon monoxide. Evidently here $n = 1$, so that each molecule of carbon monoxide occupies only one elementary space.

The writer has found that the same relation holds when these gases react with each other at very low pressures in contact with platinum (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 1162). It was also found that in the catalysis of oxygen-hydrogen mixtures by a platinum wire the velocity is proportional to the pressure of oxygen, and inversely proportional to that of the hydrogen. (More recent experiments show that this is not the usual manner in which hydrogen and oxygen react in contact with platinum even at low pressures. The factors which cause the above type of reaction have not yet been determined with certainty).

An interesting application of this theory arises in connection with enzyme action. The velocity of many of these reactions varies in accordance with Schutz's rule (see Euler, "Allgemeine Chemie der Enzyme," pp. 125, 106, and 113). Consider a reaction in which a substance A is converted into B by the action of an enzyme. Let x be the amount of B formed in the time t, assuming that the substance B is absent when $t = 0$. Let E be the amount of enzyme present. Then according to Schutz's rule—

$$x = k\sqrt{Et} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25).$$

Thus the amount of B formed is independent of the concentration of A, but is proportional to $\sqrt{Et}$.

By squaring and differentiating 25 we obtain, if E remains constant,—

$$\frac{dx}{dt} = \tfrac{1}{2}k^2\frac{E}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad (26).$$

Thus another way of stating Schutz's rule is to say that the velocity of the reaction is proportional to the amount of enzyme, is inversely proportional to the amount of B formed, and is independent of the amount of A.

It is generally recognised that enzymes are colloids on the surfaces of which reactions occur. We may thus interpret Schutz's rule as an indication that the product B of the reaction is adsorbed on the surface of the colloidal particles forming a layer one molecule deep nearly completely covering the surface. By comparing Equations 26 and 24 we see that $n = 1$, from which we conclude that each adsorbed molecule occupies only one elementary space. The reaction thus takes place only on that fraction of the surface which is not covered by molecules of B.

By Equstion 24 we should expect the velocity of the reaction to be proportional to the concentration of A, but according to Schutz's rule the velocity is independent of this concentration. This seems somewhat difficult to explain. It is, perhaps, possible that molecules of A are adsorbed over practically all the surfaces not occupied by B, and that molecules of B are able to *displace* molecules of A thus adsorbed. Let θ_a and θ_b be the fractions of the surface covered by A and B respectively. Then according to the above hypothesis we would have—

$$a_b\theta_a = \nu_b\theta_b \quad . \quad . \quad . \quad . \quad . \quad . \quad (27).$$

$$\omega = \nu_a\theta_a \quad . \quad . \quad . \quad . \quad . \quad . \quad (28).$$

Since θ_b is nearly equal to unity we thus have—

$$\omega = \left(\frac{\nu_b\nu_a}{a_b}\right)\frac{1}{\mu_b} \quad . \quad . \quad . \quad . \quad . \quad (29),$$

which is of exactly the same form as 26, and is thus equivalent to Schutz's rule.

Summary.

1. The work of the Braggs on crystal structure is reviewed from the viewpoint of the chemist, and the relation of this work to theories of chemical constitution, such as those of Werner, Stark, J. J. Thomson, and Lewis is discussed in detail.

2. It is concluded that the substances whose structures have thus far been studied by the X-ray spectrograph are not representative of compounds in general. Only polar compounds have been studied.

3. Solid polar compounds are, in general, built up of atoms bound together by secondary or residual valence. The whole crystal must be regarded as a single molecule.

4. Solid non-polar compounds consist, in general, of "group molecules" in which the atoms are usually held together by primary valence. These group molecules in turn are bound together by secondary valence to form a large "crystal molecule," which includes the whole solid mass.

5. There is no present justification for dividing interatomic (or intermolecular) forces into *physical* and *chemical* forces. It is much more profitable to consider all such forces as strictly chemical in nature. Evaporation, condensation, solution, crystallisation, adsorption, surface tension, &c., should all be regarded as typieal chemical phenomena. The object of this paper is largely to show that *chemical knowledge already available* is directly applicable to the study of these phenomena.

6. From a consideration of such properties as specific heat, compressibility, coefficient of expansion, &c., it is concluded that collisions do not take place between the atoms of solids, but that these move about equilibrium positions under the influence of both attractive and repulsive forces.

7. The "time of relaxation" of the atoms of solids is calculated approximately from the heat conductivity, and is found to be of the order of 10^{-14} to 10^{-7} seconds. An independent method by which the "time of relaxation" can be calculated from the rate of evaporation of a substance in vacuum gives substantially similar results. Thus the time necessary for an atom of a solid to reach thermal equilibrium with its neighbours is very small compared to the time necessary to make a single oscillation about an equilibrium position. The "oscillations" are thus extremely strongly damped.

8. Since solid substances, in general, are held together by secondary rather than primary valence there are few limitations to the number of compounds that can exist in the solid state. Most of these compounds do not show a composition which could be predicted from the ordinary rules of valence. Metallic compounds, minerals, solid solutions, and glasses are discussed from this point of view.

9. By considerations based largely on the compressibility it is concluded that the attractive forces between atoms usually reach a maximum intensity when the distance

between adjacent atoms in solids is increased by about $0{\cdot}6 \times 10^{-8}$ cm. (10—30 per cent of the normal distance between atoms).

10. Since energy must be expended in breaking apart a solid, the surfaces of solids must contain more potential energy than do the corresponding number of atoms in the interior. Since this potential energy is probably electromagnetic energy in the field between atoms, the interatomic forces are more intense on the surface than in the interior. This intense surface field of force (unsaturated chemical affinity) is one of the causes of the phenomena of condensation and adsorption.

11. Because of the small time of relaxation and because an atom approaching the surface is attracted by many, but later is repelled by few atoms, it follows that the surfaces of solids are almost wholly inelastic in regard to collisions of molecules impinging on the surface. There is also a great deal of experimental evidence of this inelasticity. As a result nearly every molecule or atom striking a solid surface condenses no matter what the temperature may be. While condensed it is held to the surface by forces quite similar to those holding solids together (either primary or secondary valence). At high temperatures evaporation may take place almost immediately after condensation, but at lower temperatures the condensed atom or molecule may remain indefinitely.

12. The phenomena of condensation and evaporation (sublimation) of solids is discussed at some length. In general, the rate of evaporation (m) of a substance in a high vacuum is related to the pressure (p) of the saturated vapour by the equation—

$$m = \sqrt{\frac{M}{2\pi RT}}\,p.$$

Red phosphorus and some other substances probably form exceptions to this rule.

13. The mechanism of the dissociation of a solid, such as $CaCO_3$, is discussed. It is shown that when, according to the phase-rule, separate phases of constant composition are present the reaction must take place exclusively at the boundaries of these phases. This kinetic interpretation of the phase-rule indicates clearly the distinction between reactions in which solid solutions are formed and those in which separate phases appear. This theory offers a ready explanation for the fact that hydrated crystals frequently fail to effloresce unless scratched, and for the fact that thoroughly dehydrated substances often absorb moisture with great difficulty.

14. Adsorption is a direct consequence of the time lag between the condensation and the subsequent evaporation of molecules. The adsorbed substance may be held to the surface either by secondary or primary valence. In either case it is profitable to regard the phenomena as chemical in nature. A large number of experimental results are given which prove conclusively that adsorption is very frequently the result of the strongest kind of chemical union (primary valence) between the atoms of the adsorbed substance and the atoms of the solid.

15. It is shown that the action of a typical catalytic poison depends on the formation of a very stable film one atom deep over the surface of the catalyser. The chemical activity of any solid surface depends upon the nature of, the arrangement of, and the spacing of the *atoms* forming the surface layer. There is a very close relation between the chemical activity of a surface and the electron emission from it (either thermionic or photo-electric emission).

16. A brief quantitative development of this theory of heterogeneous reactions is given. A "law of surface action" analogous to, but different from, the "law of mass action" is proposed. This theory is in accord with and affords an explanation of Reichinstein's "Constant Sum Hypothesis." An outline is given of the application of this theory to heterogeneous gas reactions and to enzyme action.

The second part of this paper will deal with the Structure of Liquids with particular reference to surface tension phenomena. It will be shown that the surface tension of organic liquids is a characteristic *chemical* phenomena. It depends particularly upon the *shapes* of the group molecules and upon the relative intensities of the chemical activity of *different portions* of the molecules. A method will be described (together with experimental data) by which the *cross sections*, *lengths*, and other dimensions of group molecules of liquids may be determined.

VEGETARIAN FEDERAL UNION.

The following memorial has been forwarded to the Food Controller :—

The Central Committee of the Vegetarian Federal Union, officially representing the many vegetarians within His Majesty's Dominions, desire to make the strongest possible protest against the various methods which have been adopted during recent years to prolong the apparent freshness of food, by impairing, destroying, or eliminating the enzymes and vitamines of food. Such practices reduce the nutritive value of food, and as a result the health, physique, and constitution of the people are impaired.

We would draw particular attention to the most pernicious practice now in force of kiln-drying or baking the grains used for making our war flour. Such methods destroy the enzymes of the grains, and result in the formation of lactic acid when war bread is eaten.

When the enzyme amylase is destroyed, before performing its action of converting starch into sugar ready for assimilation, lactic acid is produced during the process of chewing the starchy food. The ptyalin of the saliva converts starch into sugar, and acid producing bacteria, which are always present in the mouth, form lactic acid from the forming sugar, the ptyalin of the saliva and acid producing bacteria are swallowed with the bolus of bread, and the formation of lactic acid continues for some time. The lactic acid combines with alkaline bases. The neutral salts formed are excreted, and the body deprived of essentials of complete nutrition. Further, some of the lactic acid combines with the lime salts of the enamel of teeth and starts dental decay.

The enzyme cellulase of grain being destroyed, before converting cellulose into sugar, the great amount of cellulose contained in our war bread is not digested and passes unchanged from the body. War bread contains much cellulose in order to increase the amount of food. Destroying the enzymes defeats this object by reducing the amount assimilated.

Owing to so much of our war bread recently being "ropy," it was suggested the Food Ministry might during hot weather drop the regulation requiring bread to stand for twelve hours before being sold. Since then, it has been stated, this cannot be done, because the French, who regard this provision as necessary to them, might find their people making the impossible demand that they should be treated likewise. The bread of France is made from flour containing the unimpaired enzymes of the grain.

We earnestly urge that in all respects the conditions regulating our bread may be made the same as those of the French, and that the natural digestive ferments of all cereals be carefully conserved for the better digestion of such staple foods.

We further urge that the present blending of various cereals, which require different temperatures and different periods of cooking, may cease, and that the different cereals be used to make distinct breads. Such readjustment would enable our poor to obtain barley and oaten loaves at a cheaper rate than wheaten bread.

Signed on behalf of the Committee,—

Arnold F. Hills,
President Vegetarian Federal Union.

ROYAL PHOTOGRAPHIC SOCIETY.

Annual Exhibition.

The Royal Photographic Society, of 35, Russell Square, W.C., has made an innovation in its usual procedure by holding its Annual Exhibition at its own premises, instead of at one of the art galleries, and invites the public to view the photographs free of charge.

The Exhibition will be open daily (Sundays excepted), from 11 a.m. till 9 p.m., and lantern lectures on popular and interesting topics will be delivered each Tuesday and Friday evening from 8 till 9.

The Society's rooms are so spacious that the usual number of pictorial and scientific exhibits has not been curtailed. There are somewhat fewer colour transparencies due to the difficulty in obtaining supplies of plates from France, where one popular brand is made.

An interesting feature is a large series of photographs loaned by the Royal Flying Corps. These show positions held by the enemy, and, as the photographs made by flight officers have been taken at intervals, show the obliterations of the natural features of the country under heavy gun fire. Another series shows our own men drawn up for attack. In one instance the troops are seen standing at ease and later on at attention before the General in Command. Large detachments of aeroplanes guarded the troops from the enemy's flying machines.

Another series show the gradual evolution of the trench system, from the simple earthworks thrown up in the early days to the elaborate system now in vogue.

The pictorial exhibits show a remarkably high level of excellence, and in consequence of this and the absence of freak work no one picture stands out to strike the eye. Most of the well-known art workers are represented, and among them are many new men who have won recognition. The prevalence of light mounts and the absence of heavy dark frames give the whole exhibition a more cheerful look than was the case some years back. This is particularly noticeable in the continuation of the Pictorial Section on the second floor, where a selection of photographs by various three-colour processes strike a warmer note.

The transparencies (also on the second floor in a darkened room), although not so numerous as in the past, are all of good quality.

The Scientific Section (on the same floor) contains some fine natural history specimens, among them being striking portraits of many of the denizens of the Zoological Gardens photographed by Mr. D. Seth-Smith. There are many fine examples of photomicrographs, most of the producers being members of the Society or of the Photomicrographic Society, or of both. Radiographs are shown by the Cancer Hospital and others. A series of cloud forms taken for meteorological purposes mark clearly the distinction between the various types of clouds, and a series of stellar charts contributed by the Astronomer Royal, and lunar photographs by J. H. Reynolds, F.R.A.S., call for particular attention.

Medals have been awarded by the judges to H. Y. Sümmons and H. Essenhigh Corke in the Pictorial Section, to J. Copperfield in the Colour Section, and to F. Martin Duncan and the Cancer Hospital in the Scientific Section.

CORRESPONDENCE.

CUPFERRON.

To the Editor of the Chemical News.

Sir,—With reference to the recent report in the Chemical News of a lecture by Mr. A. C. Chapman entitled "Some Main Lines of Advance in Modern Analytical Chemistry," I shall be obliged if you will kindly inform me through your correspondence column, or otherwise, where I can find details of the methods of using cupferron for the purposes mentioned on pp. 270—271 of your issue of June 8 last (vol. cxv.). I beg to thank you in anticipation.—I am, &c.,

E. P. Burt, Chemist, Newburn Steel Works.

24, Tynevale Tce,
Lemington, Newcastle on-Tyne,
September 26, 1917.

COPROLITES.

To the Editor of the Chemical News.

Sir,—I shall be glad to assist your correspondent in every way if he makes an appointment. Meanwhile I would beg to refer him to the following treatise, "The Manufacture of Chemical Manures," by J. Fritsch, translated and annotated at great length by me, and published by Messrs. Scott, Greenwood, and Son.

The percentage of tricalcic phosphate in Cambridge coprolites is given there as about 70 per cent; that is far too high for the present day, and I doubt very much if it was ever attained except in unique samples or parcels. In any case the average percentage long before the collection of coprolites ceased in this country, about the latter seventies or very early eighties of last century, had dwindled considerably below 60 per cent. Unfortunately, this 70 per cent error of Fritsch has been copied by other authorities. Coprolites require somewhat fine grinding through a 50 mesh sieve at least, but they are very tractable both in mixing, storing, and breaking up. Unfortunately the supply has ceased for over thirty-five years at least. When manager of a manure works in the north of England the firm got their Cambridge coprolites from a local wholesale manufacturer with conveyance by sea. I wrote a Cambridge collector whose old circular I came across in the office with the view of obtaining a direct supply by rail. But collection had ceased, and freight alone was 25s. a ton. Finely-ground phosphates have been tried as turnip manure, but the experimenters forgot that a turnip requires sulphur as much as it does phosphorus. But very finely-ground phosphates would do very well for wheat, and if still attainable in quantity a central grinding mill for Cambridge would be a boon. All German text-books vie with each other in telling the deliberate falsehood that Liebig invented the superphosphate of the present day. He did nothing of the kind; it was invented by Lawes and Gilbert. What Liebig recommended was something which he did not invent at all, viz., the solution Fourcroy and Vauquelin used in the making of phosphorus, and so dilute that it would take a tank the size of a gasometer to manure a 25 acre field! and it would take a *Great Eastern* to convey Liebig's liquid manure equal to 100 tons of superphosphate. Liebig's slops are not in it.

No British chemist has ever pointed this out. Too many of them are German Ph.D., and to them the memory of Liebig is dear, a most as dear to them as the degrees which even those in State-aided colleges still delight to sport and flaunt and flounce in the face of the President of the Board of Education and the Treasury, to say nothing of a discerning public.—I am, &c.,

"Donald Grant."

P.S.—"Donald Grant," the name I gave on the title-page of Fritsch's book, is a *nom de plume*—the Editor has my real name and address, but if a personal interview is desired I must have a day's notice.

MEETINGS FOR THE WEEK

Tuesday, 16th.—Institution of Petroleum Technologists, 8. "Testing and Standardisation of Motor Fuel," by E. Lawson Lomax.

Wednesday, 17th.—Society of Glass Technology, 3.15. (In the Physics Lecture Theatre, the University, Sheffield). "Use of Semi automatic Glass-making Machinery in America," by R. E. McCauley.

THE CHEMICAL NEWS

Vol. CXVI., No. 3021.

THE
MANUFACTURE OF NITRATE OF AMMONIA BY ELECTRIC POWER AT COKE-OVEN PLANTS.*

By E. KILBURN SCOTT, A.M.I.C.E., M.I.E.E.

(Concluded from p. 172).

Estimate of Cost.

We will assume the electro-chemical plant is of such size as to utilise 1000 kw., the round figure above mentioned, which the power-house will supply continuously.

The factory will be equipped with the three-phase furnaces and boilers, switchgear and instruments, fans for air supply and circulation of gases; apparatus for cooling and oxidation of gases, also the acid and alkali absorption towers or chambers, complete with acid elevators and distributors; reservoirs and mixing tanks; evaporators, crystallising and drying apparatus, &c. A convenient method of arriving quickly at an over-all price commonly used for electro-chemical plants, is to take a price per kilowatt. £8 is a fair price, so the total is £8000.

The price of electrical energy is assumed at ⅛d. per unit, which is fair, because electro-chemical factories in this country have been supplied with electric energy at under that figure for many years.

The number of working hours in a year—namely, 8000—is convenient because it leaves a balance of 760 hours for overhaul time, &c., and thus less spare plant is required. It also allows for intermittent running off the peak in winter, if found necessary.

Depreciation on the electro-chemical plant may be taken at 10 per cent, this being sufficient to pay for a new plant in about seven years. It should be noted that a large proportion of the capital cost is required for absorption plant which is largely of brickwork, and for which the depreciation might be taken at 2½ per cent.

The yield of acid is reckoned at 1½ tons of 33 per cent nitric acid per kilowatt year—that is to say, 1500 tons from a plant utilising 1000 kw. This is based on a yield of 66 grms. of concentrated acid, or 200 grms. of 33 per cent acid per kilowatt-hour, thus—

$$\frac{200 \text{ grms.} \times 1000 \text{ kw.} \times 8000 \text{ hrs.} \times 2{\cdot}2}{100 \times 2240} = 1500 \text{ tons.}$$

As a matter of fact greater yields are obtainable, but the above figure is sufficient for the purpose and to show the sequence of the calculations.

Working Expenses.—Assuming the electro-chemical plant to cost £8000, and to utilise 1000 kw. for 8000 hours per annum at ⅛d. per unit, the expenses are—

Electric energy, $\frac{1000 \times 8000}{240 \times 8}$	£4166
Depreciation 10 per cent on £8000	800
Salaries, wages, stores royalty, &c... ..	1790
	£6756

This, for an output of 1500 tons, gives £4½ per ton of 33 per cent nitric acid, the equivalent rate for pure acid being £13 10s.

For a plant to utilise ten times the amount of energy, or 10,000 kw., the cost should be much less, even taking the above figures for the yield.

The amount of ammonium nitrate that can be made by such a plant is shown by the equation and atomic weights thus—

	NH_3	+	HNO_3	=	NH_4NO_3
With pure acid..	17	..	63	=	80
With 33 per cent acid ..	17	..	189	=	80

Inserting 1500 tons of acid instead of the figure 189, we get 125 tons of pure ammonia plus 1500 tons of 33 per cent nitric acid gives 635 tons of pure ammonium nitrate.

As to the value of ammonia from the coke-oven gas, the author takes the figure mentioned at the beginning of this paper—namely, £30 a ton, or 3¼d. a lb. It is surprising how opinions differ on this simple matter. Many accepted electrical calculations, which really do involve detailed consideration, and yet quibble as to the value of ammonia. As a rule they go wrong by taking the ruling price of sulphate of ammonia and deducting the price of ammonia from that. It is perfectly obvious that this is incorrect, because no one would make ammonia from such a finished manufactured product.

Cost per Ton.—The cost per ton may now be set out as follows:—

1500 tons of 33 per cent nitric acid at £4½ ..	£6750
125 tons of pure ammonia .. .. at £30 ..	3750
	£10,500

As this produces 635 tons of ammonium nitrate, the calculated cost is therefore—

$$\frac{10{,}500}{635} = £16\tfrac{1}{2} \text{ per ton.}$$

In addition to ammonium nitrate, there is also the sodium nitrate-nitrite. This may be assumed at 1-10th of a ton per kw. year, and it is readily saleable. It should be worth £1500 a year.

Price.—Before the war, nitrate of ammonia made by the electric process in Norway, was sold in large quantities at £28 to £32 a ton. Properly speaking, there is no quotation now, because all the make is taken by the Government for explosives. Its minimum price may, however, be fairly taken at double the above figure.

What will happen after the war we cannot tell, but one thing is certain—namely, that the price per unit of contained nitrogen will be higher for nitrate of ammonia than any other nitrogen compound. This has always been so, because the combined nitrogen is 35 per cent.

Usual percentages of combined nitrogen are given in the following table:—

Name.	Symbol.	How obtained.	Usual p.c. of nitrogen.
Sodium nitrate.. ..	$NaNO_3$ ..	From Chili ..	15½
Sulphate of ammonia	$(NH_4)_2SO_4$	By-product of coal	18
Calcium nitrate.. ..	$Ca(NO_3)_2$	Made by electric power	13
Calcium cyanamide ..	$CaCN_2$		18
Nitrate of ammonia..	NH_4NO_3		35

As a means of transporting combined nitrogen from one part of the world to another, nitrate of ammonia is better than any other medium, so it is likely to always hold the field in the export market.

Uses of Nitrate of Ammonia.

Nitrate of ammonia is the principal ingredient of most safety mining explosives, the word "safety" being a relative term expressing the fact that they are safer than dynamite, &c. On the Continent, before the war, nitrate of ammonia explosives were considered so safe that they were carried on railways at ordinary rates. This, no doubt, had much to do with nitrate of ammonia explosives being adopted more quickly than with us, for our railway authorities have always insisted in charging at the high rates.

The British and certain other governments have passed regulations insisting on only safety or permitted explosives eing used in mines. The more this idea extends the more nitrate of ammonia will be required.

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* A paper read before the Coke Oven Managers' Association (Midland Section), July 28, 1917. From the *Colliery Guardian*, August 3, 1917.

Other uses of the nitrate are: in burster charges for shells; as an explosive for tree planting; and as a fertiliser.

Importance of Home Manufacture.—Before the war practically all the nitrate of ammonia used in this country for making safety explosives for mining, &c., was imported from Norway, which, considering the necessity for nitrate of ammonia, is another instance of the absurdity of allowing foreigners to control businesses important to the nation.

Norway had no coal from which to obtain ammonia, and so the ammonia had to be sent from England. Ammonia liquor was collected from gasworks and coke-oven plants, and concentrated to bring the ammonia up to 25 per cent. The solution was then railed to Hull, shipped in steel tanks to Skien in Norway, and carried a considerable distance up country to the air nitrate factory.

As the proportion of water was 75 per cent, the freight, calculated on the real ammonia in the solution, was naturally high. The cost of carrying steel tanks to and fro, and the heavy depreciation of them, was also a great expense. Finally, the nitrate of ammonia when made was brought from Norway to this country, a great deal of it going to Nobel's works in Ayrshire.

Since the war ammonia liquor has continued to be sent to Norway, and nitrate of ammonia brought back, but since the submarine menace this business has practically stopped. Ammonia is now being made in Norway by acting on calcium cyanide with superheated steam in autoclaves, but the Norwegians prefer our by-product ammonia as being cheaper.

Before the war Germany was the largest purchaser of Chili nitrate, taking twice as much as the next consumer, the United States, and over six times as much as this country. Now Germany does not require any Chilian product, because immense plants to make nitrates from the air have been established. As a matter of fact, this air nitrate development ranks as the most remarkable scientific achievement of the war.

It will easily be seen that by making nitrates from air the Germans are at a great economic advantage, for our complete dependence on Chili nitrate means we have to pay large sums for the nitrate and for transport, insurance, &c. Also there is part of the immense national charge for protecting the sea routes by which we get it here. Large sums are also required for the pyrites, sulphur, and for the plants to manufacture sulphuric acid with which to treat the nitrate.

DISCUSSION.

The PRESIDENT, in inviting discussion, said Mr. Kilburn Scott had opened their eyes to something they did not know of. His paper had been most interesting and of very high educational value.

Mr. B. W. HAIG said that Mr. Kilburn Scott had made a very good case indeed of what he had set out to show. There were doubtless many coke-oven installations in Yorkshire quite large enough to run successfully such an installation as had been described. The paper covered a very wide field, and there were certainly many points upon which they would like to hear a good deal more before they put themselves in a position of recommending their firms to embark upon so large a project. Mr. Kilburn Scott's remarks as to the comparative costs of power derived from steam and gas engines in themselves would have made a valuable paper, and he (Mr. Haig) wished he had come prepared with figures to suggest some questions on this matter. It was somewhat surprising to hear that colliery proprietors could value their power as nothing, in view of the fact that certain coke-oven people were selling their gas at very good prices; and whilst he was not prepared with figures on which to challenge those advanced by Mr. Kilburn Scott, the production of power at ⅛d. per unit certainly struck him as a very low estimate indeed. It would have to be a very large unit in which the process could be profitably adopted. There would have to be highly skilled officials in the electrical department, in view of the danger of using such high voltages as suggested. Most coke-oven plants would not at present have such men on their staff, and the amount put down for salaries and upkeep seemed to him to be on the small side. The technical descriptions given had certainly been most interesting, and it would be interesting to know if there was any such plant in existence in England which could be inspected. With regard to the purity of the product, some of them already made or were going to make concentrated ammonia liquor, and one of their troubles was to get rid of the sulphur compounds, and he was wondering whether they would have a very detrimental effect on the resulting ammonium nitrate. He presumed the sulphur would be precipitated and lower the quality of the ammonium nitrate, and possibly make it dangerous for use. In conclusion Mr. Haig formally moved a vote of thanks to the author.

Mr. G. A. HEBDEN said some eight or nine years ago he had a somewhat similar experience as that of which the author had spoken in connection with calcium nitrate which his firm used to import from Norway and make into bicarbonate of ammonia, mixing the calcium nitrate and making pure ammonium nitrate with it, and he was surprised that the alkali people had not taken up such a simple process. He believed the calcium nitrate could be converted into ammonium nitrate quite easily, and the waste CO_2 utilised with ammonia to make ammonium bicarbonate. It would have been done in England but for the fact that the Norwegian people paid more for the ammonia, and it was still being sent out of this country. They were shipping ammonia of 900 specific gravity, 28·3 per cent.

The PRESIDENT asked if the electrodes in the arc flame furnaces described should be of any particular metal. Had the choice of any special material—aluminium, copper, &c., or any special alloy—any bearing upon the process? With regard to plants in course of erection he had heard from a friend that there was a plant of similar description working in South Russia. He would also like to know if there was any possibility of synthetic ammonia being produced by such a process.

Mr. KILBURN SCOTT in replying to the discussion, agreed that a number of coke-oven proprietors were doing very well by the sale of the gas, but he thought it very likely that a number of the beehive type of ovens—of which there were, he believed, 16,000 in this country—would be done away with. In future coke would be made on a very much larger scale than at present, and the Government would surely compel the use of coal in this way and stop its being wastefully used, as at present, in boilers by direct burning. When new plants were put down and beehive ovens abolished there would be a tremendous amount of power, in the form of gas, available, and it was to utilise some of that gas that he had suggested the process described. Where coke ovens were near a town then doubtless it would pay them better to sell some of the gas for illuminating purposes, &c.; but a great many installations would be remote from such centres, and in such cases the better plan would be for coke-oven proprietors to establish their own power-house, make their own acid, and produce nitrate. He believed that the only electric furnace at present producing nitric acid direct from air in this country was his own. A factory was to be built in Manchester, but it would be some time before it was completed. It was because the nitric-acid process had been hanging fire so long that he had taken the opportunity of putting his views before such a society as theirs, and he was very glad there was such a society to receive the suggestion so sympathetically. With regard to the sulphur compound, the ammonia that went over to Norway had the sulphur carefully removed. Ammonium nitrate for making burster charges must be very pure, but when it came to be used for fertilisers and certain other purposes after the war, there would not be the need for such absolute purity. It could be made certainly without the high concentration needed (in order to save freight) in that now sent to Norway. The Norwegian calcium nitrate was made electrically, and some of it was converted into nitric acid in this country, and also used for making ammonium nitrate. If we had had the furnaces here, then this roundabout process would have been avoided. The trouble with nitric acid was that it could not be carried any distance, especially by sea. Ammonium nitrate would always have a big field for export, because it could more easily be conveyed in concentrated form—viz., with 35 per cent of fixed nitrogen. It would in future be the standard method of carrying nitrogen from one part of the world to another. With regard to the president's enquiry as to the electrodes, these were made of aluminium alloy and copper alloy. The metal used certainly had a most important bearing. Some claimed that there was a catalytic action going on in the furnace, but the whole explanation of the formation of free nitrogen and free oxygen in the electric arc was obscure. Some chemists maintained it was purely thermal, but he was satisfied that this was not so, though a high temperature might be favourable to the yield. He believed it was due to the collision bombardment of electrons. Whilst he wanted to see the particular method to which he had devoted years of study given a fair trial, he was anxious that all processes should be tried, so long as this country would be placed in a better position to produce its own nitrate. The problem was being tackled in various places, but investigators were all working in their own separate pigeon holes, so that progress was slow. He pleaded for more sympathetic co-operation and encouragement on the part of the Government, as this was a matter of great national concern. It was time the country had at the heads of its technical departments men who understood the needs of the situation better than lawyers, medical men, &c., could be expected to. Germany put at the head of its Munitions Department the head of the biggest electrical concern in the world, and the result was that that country was now independent of Chilian nitrate.

The vote of thanks was seconded by Mr. J. T. Price, and heartily accorded.

THE REJUVENATION OF EARTH AND MAN.

By SAMPSON MORGAN.

Is the earth in its dotage? Have its vital and productive powers declined and fallen into decay? Let us see.

The cooling of the earth's surface when it reached the stage suitable to the advent of organic forms, marks one of the most remarkable epochs in the whole history of biology. The consummate material order in the universe, even to the most minute details, shows, to my mind, the existence of a consummate moral order.

"It cannot," as one writer says, "be blind gravitation and affinity that were able to bring forth and adapt all this." The most reasonable explanation appears to be, that matter, mind, and life are one, and that matter being intelligent exercised the powers it possessed of transmitting life to organic forms here, when the declining temperature of the earth's crust fitted it for their appearance. The demonstration of science that life can only come from life is unassailable, yet there is no great gulf between the living and non-living, as Prof. Huxley suggested there was. Prof. Drummond not only agreed with Huxley, but claimed that a barrier exists which separates mind from matter.

But there is no "missing-link" in the chain of argument to the contrary, for it was forged by nature and is perfect in every detail. Life is not, as Prof. Drummond said, a bending down to but an uprising from the inorganic world. The vital thread in eternal continuity runs through the organic and inorganic spheres. It was the universal, inherent, intelligent tendency which particles of dissimilar bodies have to combine and form new compounds and structures which, under the resistless and restless moulding influence in Nature, first transmitted life through lowest organic forms to earth.

The oneness of the world is undoubted, and we are part and parcel of it. Life is a continuous series of changes, not only in this world but in every sphere everywhere. There is no death, only a transformation in the form of matter. If microbes, mammoths, men, worlds, and systems disappear from view they do not die. They are still subject to the law of cohesion, or close union of parts, and continue, in some form or other, to maintain their uninterrupted connection with the unbroken texture of the visible or invisible universe which is eternal.

Wherever history throws its illuminating beams upon the acts and thoughts of men it discloses to us the fact that in every age the pessimist was as much in evidence in the past as in the present. "Persistent and over cultivation of the soil has seriously affected its vital and productive powers. The earth is played out," and so on, they said in the days of Homer, and the gloomy views are upheld to-day in many quarters.

Seneca spoke of "the senility of the soil." Hehn refers to the discreet opinions of Franz Unger, who, in refutation of the pessimists in fertility, practically said there is no such thing as the senile marasmus of Nature. "The ground has lost nothing of its creative fire In its subjugation and improvement it only requires assistance." Brains count more than brawn. Change and improve the men who inhabit and till the ground and the earth will smile through such bumper harvests of glowing fruits and golden grains as few of our cleverest thinkers conceive possible.

Nevertheless, some of the opinions of Hehn himself in this connection are pessimistic and erroneous. I insist that the golden age of soil productivity in Europe, Asia, and Africa is not behind but before us. Clean culture, Nature's method, is capable of making the miasmatic swamps of the tropics as sweet and healthy as England, and the huge deserts even of Africa fertile beyond description.

In expressing my views on the subject to an ex-admiral of the British navy, who is now interested in the intelligent cultivation of his own estate, he replied, "You are perfectly right, I am sure, of the enormous importance of your clean culture method to the tropics."

A distinguished West Coast African treaty maker whom I saw at the Colonial Institute was quite enthusiastic over its value, and in a long interview expressed the opinion that it would do more than anything he knew of to develope lucrative food producing industries there. He paid me the compliment of saying, "You are the first man I have met who understands the situation. You are right; Western Tropical Africa may be made a grand and healthy field of activity for white labour by clean culture. I do wish you would come with me to the West Coast when I go next month."

He fully agreed with me as to the tremendous possibilities of the West Coast as an agricultural El Dorado for the world.

Darwin, Henslow, and Clean Culture.

Whilst the Darwinians say that a plant survives because of some superiority in the structure of its flower, Prof. Henslow says that a seedling survives because it is vigorous. But he stops short at the most critical point in the argument. Like the Darwinians, he fails to see that though the survival of the fittest is the survival of the most vigorous, the survival of the most vigorous is the survival of the best fed. I therefore hold that both Darwin and Henslow overlooked the chief force in the situation. Bacon was nearer the truth then either of them. There is no Natural Selection no more than there is any unsurpassble gulf separating the organic from the inorganic, or man from the lower mammals. Food ever was and will be the basis of progress or of retrogression in the mineral, vegetable, and animal kingdoms.

What are the most perfect plant foods for soils and crops? Is it possible to maintain fertility under heavy persistent cropping with forcing chemicals and carbonate of ammonia laden manure, or must we depend upon the provision of the original constituent elements?

Before these questions can be answered properly we must recognise that there is an affinity between the soil and the plant and tree. We must admit that the wood of trees, the flesh of fruits, and the tissues of roots and grains are composed of the same elements as the soil in which they are grown. We eat the elements of the plant foods fed into the fruit, root, and grain, and as man is what his food makes him so the products of the earth are what their food makes them also. There is no difference.

Some experts claim that cultivation alone will maintain fertility indefinitely. Others that green manuring in some form will suffice, and many that dust of the disintegrated rock will furnish the one thing needful. Though some of our greatest geologists assert that the original soil consisted of disintegrated rock, they overlook the fact that soil is not made up of rock exclusively. The late Prof. Thorold Rogers said, "Wheat will not grow on a granite rock, but if this rock be disintegrated it makes the most fertile soil." But does it? The disintegrated rock formed the basis of the soil in the beginning but no more. Soil consists of vegetable and mineral amalgamations, and only with such is it possible to enjoy perfect crops and perfect products.

The physical degeneracy observable on every hand, both in country and town, is mainly due to the persistent consumption of foodstuffs which have been imperfectly grown, and are thus incapable of nourishing the body. Analysis of the flesh of animals, roots, fruits, and grains proves that under existing methods of production 75 per cent of the internal structures are weak, watery, and unhealthy, and consequently unfitted to fulfil the purpose for which they are utilised. Animals, roots, fruits, and grains, fed with weak disease engendering "foods," cannot possibly produce vitalising robust tissue, and such when consumed is incapable of elaborating disease resisting tissue in man.

I have in my experiments with plants and soils demonstrated the positive affinity between perfect food and health, and imperfect food and disease. Since then Prof. Potter, in a paper at a British Association Meeting, endorsed clean culture in my words as follows:—"Susceptibility to disease is influenced by manural treatment in the vegetable kingdom, and high fertilisation with nitrogenous manures lowers the power of the plant or organism to resist infection."

Before bacterial disease in the vegetable kingdom can be effectually dealt with these facts must be recognised openly and generally. The maintenance of fertility in the soil is due to the unimpeded activity of minute organisms. Their activity depends upon congenial conditions and perfect food. The laws of Nature dominate the life of the microbe as well as that of the mammoth.

Chemical analysis has demonstrated that in wheat growing countries the quality of the bulk of the grain produced is of low food value. The two kinds of wheat, *Triticum durum* and *T. vulgare*, offer us object lessons well worth consideration. The former is hard, the latter soft. In soft grains the water percentage ranges from 10·0 to 16·0, and in hard grains from 5·0 to 10. In soft wheat the starch percentage is 65·0, in hard it is 48·0. The gluten percentage in soft wheat is 10·0, in hard wheat it is 19·0.

The soft wheat contains more water, more starch, and less gluten; the latter, of course, being of the utmost importance in building up health of body and brain. The flinty grain cannot be grown to perfection with carbonate of ammonia laden manure. The agricultural chemists cannot maintain the hard flinty glutinous character of wheat grains by the present method of fertilisation.

The latest results, secured at one of the leading Experimental Stations in the United States, led to the conclusion that gluten is the most important constituent of wheat flour, because it makes possible the baking of light bread, and that the gluten content of flour depends upon the protein content of the wheat from which it was ground. Thus those wheats which establish the standards of excellence in milling centres are relatively high in protein, and produce flours of relatively high gluten content.

Practically it is admitted that the objects of the wheat breeder are valueless if the protein content is materially sacrificed. Again, I insist, that only by the use of mineralised humus can the high protein content, essential for the production of perfect crops of perfect wheat grains of high protein percentage, be obtained.

Plant breeding and selection may produce higher grades of wheat in the future as they have done in the past, but to what end, since, if the soils in which the grains are grown are fertilised with manure and forcing chemicals, they will in a few years run out and degenerate to the ordinary unsatisfactory level. Macaroni wheat is a perfect type of wheat, and the softer fleshed home-grown wheats can be brought up to its level, provided clean culture fertilisation is utilised.

Experiments in California have proved when oranges were fed with nitrogenous manures, the sugar contents of the fruits were reduced, the flesh became of coarser texture, and the amount of juice declined. It was also shown that they delayed the period of ripening and lowered the keeping qualities of the oranges. All manure fed fruits are affected in these ways, as I have proved and explained for years.

The Earth Bonfire Ash.

That the world came through a titanic conflagration, a huge celestial bonfire, and that the crust of the earth, with its rugged ranges of sky high mountains, is the resultant residue of the burning, few will attempt to deny. In due course it reached its meridian, then began to decline, leaving a conglomeration of solidified ash in the form of the outer coatings of the earth as its residue.

First, there was the gaseous burning state, then the melting or liquid state, and, finally, the cooled or solid state. The hard mineral crust formed on the earth, in what is termed the "third stadium" of the world's formation, brings us to the time of the consolidation of the rocks, such really consisting of ash in compressed form.

No sooner had the structure of the earth been completed than mighty forces of Nature were set in motion, grinding down the face of the iron clad rocky crust into particles so fine and dust-like that they could not be seen by the human eye. These dust-like mineral particles together with decaying vegetable matter formed the first soil.

Though in some forms of sedimentary, organic, and igneous rocks we have ample materials of undeniable importance for fertilising purposes, possibly granite, a crystalline rock of considerable beauty, is the best for enhancing soil fertility and enriching all crops naturally. There are enormous ranges of granite masses in Wales, Cumberland, and Scotland, for instance. In the lowest layers of the earth's crust incalculable quantities exist, formed possibly mainly in the Azoic age.

So immense are the masses of rocks beneath our feet that it is impossible to get down to the bottom of them. Nevertheless, thanks to the titantic upheavals which have taken place under the tremendous influences of the irresistible forces of Nature, colossal hills and mountains of granite have been forced upwards through the earth's crust into the air, in some instances reaching such a height that their peaks look as if they would pierce the skies.

In these masses we have offered us by Nature the most perfect form of mineral plant food for all crops that it is possible to obtain. All that is needed is to grind down these blocks of solidified dust to fine powder, which, when mixed with uncontaminated vegetable humus making material, furnishes the most perfect combination that can be fed to the soil.

According to my clean culture teaching, bonfire ash is one of the mightiest factors, not only in the production of perfectly healthy worlds but of perfectly healthy soils, vegetable and animal cells, beneficent bacteria, grasses, plants, trees, mammoths, and men.

The new earth—that is, the clean earth—lies at the basis of all perfection. The soil has been fouled with the filth of civilisation. Incinerate it, and what charming scenes and surroundings would be brought about. The importance of purification by fire has been ignored too long, at least by Western nations. The ashes from these fires are of untold value to the cultivator of the soil, and by ceasing to poison the earth by souring it with foul smelling "plant foods," and by letting in the light air and sun, and mineralising it with the sweet refuse of these burnings and with granite dust, we should soon increase the productive powers of the earth a hundredfold.

Exhaustion by culture is a contradiction in terms. The thing is impossible. Soils are not impoverished by culture but by the want of it. Millions of acres of unproductive land in Britain are crying out for the bland non-forcing mineral which I commend. One authority estimates that one river alone carries annually 150,000,000 tons of dissolved rock materials to the sea. Science has performed wonderful feats. It has even picked up sounds and photographed them. Would that it could separate and pick up the fine particles of fertilising rocks, billions of tons of which the mighty rivers have been permitted to carry away from the land and fling into the depths of the mighty deep.

In experiments, by digesting powdered felspar, hornblende, and other minerals with water for a week, from a third of 1 per cent to 1 per cent of the mineral was dissolved out by the water. The opinion that granite because of its hard texture is of little use in modern land fertilisation has no foundation in fact, as the above shows.

The ordinary farmer and gardener know little about the dissolving properties of rain-water, or understand that the presence of simple particles of the primary rocks in the cultivated soil are necessary to assure the elaboration of healthy supple tissue in the animal organism, or flexibility in flax, in the stem or grain of grain bearing plants and the branches of fruit trees.

The potassa in the granite is worth its weight in gold to the English and Irish flax growers, who cannot by any possibility produce that pliancy of thread which is the chief characteristic of flax of the highest commercial quality. It is utterly impossible to grow supple flax of the finest grade with carbonate of ammonia laden manure or forcing chemicals.

French, Spanish, and Irish linens lack suppleness, fineness, and durability, due in the first and second cases to an excess of lime, which makes for brittleness, and in the third case to an excess of manure, which makes for weakness in plant tissues. Suggestions for increasing the flexibility of the blood vessels of the human body will be found in my paper on "Fruits for Health, Strength, and Longevity" in the *Fortnightly Review*.

Andrew Knight and Charles Darwin both held that excess of food was the most powerful factor in plant variation. It is certainly not the vital factor in plant progress, for excess of food in either the vegetable or animal kingdom makes for sterility rather than fruitfulness.

Prof. Bailey says, "The richer the soil in available plant food the stronger will the products be." I doubt it. Life-long experimentation has taught me that an excess of plant food tends always to the demoralisation of plant tissues and of the productive powers of soils.

On one acre of pasture clean culture fed a bullock can be kept and fattened without the purchase of feeding cakes and such like, whilst on the majority of farms three acres are necessary, even with the addition of cake, and on others, again, five acres will not suffice for the purpose. This scandalously wasteful system has been permitted to continue for generations. The only remedy for this state of things is the standardisation of cultivation, the necessity for which I have insisted upon for years. A Welsh gentleman farmer has written testifying to the remarkable manner in which clean culture has improved the nutrient quality of his pastures, increasing the milk and cream output and improving the quality of both.

The Golden Rule of Sanitation.

Sir Benjamin Ward Richardson, the great authority on health, and his friend, Sir Edwin Chadwick, the well-known sanitarian, would not have written as they did in favour of fertility through sewage and farm-yard manure, both soil sourers and poisonous, had they seen the new circle of life which I have put forward as the basis of my clean culture theory.

"The sewage to the land," said Sir Benjamin, "is the golden rule of sanitation." I doubt it. Do you eat these cabbages yourself, I asked the engineer of a sewage farm who managed the steam plant and crops. "No, indeed. I sould be very sorry to; I sell them." He knew more about the real golden rule of sanitation than he did about the golden rule of morals.

The man who first introduced the dust destructor to civilisation deserves a statue of gold to his memory. He did more to lead humanity back to actual First Principles than did Herbert Spencer. The reduction of the whole of the filth of civilisation to purified ash will mark a tremendous step towards the advent of the greatest of all ages—the clean age.

THE DETECTION OF ADDED WATER IN MILK.*

By HALSEY DURAND.

The extreme variability in the fat and water content of milk has necessitated the establishment of very low standards for fat and total solids, the standard in New York being 11·50 per cent total solids, 3·00 per cent fat, and 8·50 per cent solids-not-fat.

König, in "Chemie der Menschlichen Nahrungs und Genusmittel," gives the results of 800 analyses of cow milk as follows:—

	Total solids.	Fat.	Solids-not-fat.
Minimum ..	9·68	1·67	8·01
Maximum ..	19·68	6·47	13·21
Mean	12·73	3·64	9·09

A very valuable paper has been prepared on the composition of milk by Brown and Ekroth to be presented at this meeting.

Assuming a sample of milk to be of the maximum quality, it will be seen that a large amount of water may be added and a large amount of fat removed and still be within the legal standard. From this it becomes apparent that a method for the accurate detection of added water in milk would be of the greatest value.

Two methods have been proposed, viz.:—

1. The determination of the refractive index of the serum.

2. The determination of the freezing-point of the whole milk.

A third method may also be mentioned, viz., the determination of the specific gravity of the whole milk and of the serum. This method has been in use for many years.

The first method consists, without going into detail, of the coagulation of the milk by acetic acid of known strength, and the determination of the refractive index by the immersion refractometer, and comparing the results with standards determined for whole and adulterated milks. This method has been very carefully tested out in the Department of Health Laboratory, New York. It has the advantage of speed, a very important factor when a large number of milks are run each day. It has been ound, on the other hand, to be unreliable for the detection of less than 10 per cent of added water, which is decidedly too great a margin.

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* Presented at the Annual Meeting of the American Chemical Society, New York City, September 27, 1916. From the *Journal of Industrial and Engineering Chemistry*, ix., No 1.

The second method, depending on the elevation (by added water) of the freezing-point above the normal established for whole milk, is deserving of careful consideration. This method is incorporated in the Legal Standard for Queensland:—Solids-not-fat, not less than 8·50 per cent; fat, 3·30 per cent; total solids, not less than 12·00 per cent. Its freezing-point shall not be higher than 0·55° C. below zero.

The work of the Department laboratory was carried on after the method used by Henderson and Meston in their excellent article, "The Freezing-point of Milk," published in the Chemical News (1914, cx., 259). It was found that the form of apparatus suggested in the above paper did not give uniform results with milk of known purity. This was found to be due to the fact that the tube in which the milk was frozen was not provided with an outer tube, to form an air jacket, and thus did not permit of a uniform undercooling. A Beckmann freezing-point apparatus was substituted, and a considerable number of milks were run, and very good results were obtained. All results were run in duplicate as checks in such delicate work are an absolute necessity. In the writer's opinion the method is an excellent one, but requires the most careful manipulation and constant attention in the preparation of the freezing mixture, the degree of undercooling, the stirring, and the setting of the thermometer. The great objection to this method is the length of time required for its completion. In the Department laboratory it was found that the average time required for a duplicate determination was not less than forty-five minutes, a time which would render the method impossible for a routine laboratory.

The fact that the serum of whole milk is constant, having been established by the foregoing methods, the writer has sought for a rapid and trustworthy means of determining changes brought about by the addition of water.

The first method tried was the addition of a weighed amount (3 grms.) of anhydrous lead subacetate, the reagent used in Horne's method for sugar analysis, to 100 cc. of milk, filtering the clear serum from the coagulum, and the precipitation of the lead dissolved by 25 per cent sulphuric acid with addition of alcohol. The lead sulphate is then filtered in an alundum crucible, washed with alcohol, ignited, and weighed. It was conjectured that the serum being constant a definite amount of lead subacetate would be dissolved, and that this amount would be increased by the addition of water. This proved to be the case, but the results were unsatisfactory as the filtration was very slow, and even after a number of washings an amount of soluble protein was retained by the precipitate, which resulted in a reduction of the lead sulphate. The same result was obtained on using 3 grms. of normal lead acetate.

The second method tried was the addition of 2 grms. of finely-divided silver nitrate to 100 cc. of milk, and the determination of the silver dissolved in an aliquot part of the serum by titration with N/10 thiocyanate solution, using ferric alum as indicator. This method has proved very satisfactory as far as rapidity is concerned, but a sufficient number of determinations has not been made as yet to establish its applicability.

A third method has suggested itself to the writer, viz., the coagulation of the milk by non electrolytes, such as saccharin, rennin, &c., and by electrolytes, as lead acetate, silver nitrate, &c., and the determination of the electrolytic conductivity of the sera thus obtained. As the proper apparatus is not at present available this investigation has not been undertaken. It is the intention to perform these experiments in the near future, with the belief that the problem may be solved in this way, and a rapid and accurate method for the determination of added water in milk be established.

AN INVESTIGATION OF COMPOSITION FLOORING.*

By R. R. SHIVELY.

In 1867 Sorel (*Comptes Rendus*, 1867, lxv., 102) found that a very hard material might be produced by mixing magnesia and a solution of magnesium chloride and then allowing the mixture to stand for some time. Sorel concluded that the compound which was formed possessed the following formula: — $MgCl_2.5MgO.12H_2O$, or $MgCl.OH.4Mg(OH)_2.12H_2O$. The investigations of Sorel initiated considerable inquiry, mostly by French and German chemists, but there has been a diversity of opinion regarding the exact composition of the product. (Bender—*Z. Anorg. Chem.*, iv., 644—assigned the formula $MgCl_2.5MgO.14H_2O$, or $MgCl_2.9MgO.24H_2O$; Davis—Chem. News, xxv., 258—reported $MgCl_2.5MgO.13H_2O$, while Krause — *Ann.*, clxv., 38 — decided upon $MgCl_2\ 5MgO.18H_2O$ as the correct formula).

During the past twenty-five years Sorel cement has been extensively employed with success as a cementing material for so-called "composition flooring." According to European practice, the magnesia, mixed with various "fillers," such as sawdust, sand, terra alba, infusorial earth, or asbestos, and coloured with different inorganic colours, is made into a "mortar" by the addition of a solution of magnesium chloride; the material is then applied to the floor and levelled, and, after standing several hours, it is carefully trowelled. After eight or ten hours the cement sets and the surface of the flooring is then usually treated with a coat of oil, after which the composition is ready for use.

It has been found that suitable preparations of this type make ideal compositions for floor, base, wainscot, and stairs. When carefully prepared the composition is permanent, firepoof, and waterproof, and it can be applied upon wood, concrete, or iron base in a plastic form, giving a smooth, continuous surface. The wainscot may also be made from the same material, thus forming a perfect seal between the base and wainscot, and giving a floor devoid of cracks. Any colour shade may be produced with the exception of pure white, and very attractive effects may be obtained by using borders of different colours, a mosaic design, or a narrow strip of another colour around the floor a short distance from the wall. Moreover, the mixture is little affected by heat or cold, having a very low heat conductivity, and the floor produced therefrom does not impart a feeling of coldness to the feet; furthermore, its absorption of water is very small, and it is accepted by insurance companies as fireproof.

The composition is usually applied in two coats: an under fibrous coat about 5/16 in. thick, and an upper coat containing less fibre, from 5/16 to ½ in. thick. The under fibrous coat imparts elasticity to the material and renders the floor noiseless and pleasant to the tread. In fact, this composition does not give rise to the fatigue experienced from the use of stone, cement, terrazo, or other hard floors. Furthermore, even when trowelled to a very smooth surface, this composition does not produce a slippery floor. These advantages, along with the facts that the composition costs less than tile, marble, &c., and that it will outwear eight or ten applications of linoleum, have made it a very popular floor material in Europe, especially in Germany and England.

Composition flooring of the general type described above was introduced into the United States a short time after it came into favour abroad. American manufacturers have, however, experienced considerable difficulty in the use of Sorel cement. Some have attributed this to the differences in the climatic conditions of Europe and America, the contention being that the sudden changes of temperature encountered in the United States are not experienced abroad, particularly in England and Germany. Others have expressed the opinion that the principal cause of the failure in this country is attributable to the mixtures employed; the assertion has been made that the mixtures in use here have been neither scientifically nor even carefully prepared. Inasmuch as many of the floors examined by the author are as perfect as could be desired, he is inclined to favour the latter explanation. If the trouble is due to the sudden climatic changes, why should one floor be affected and not another in the same locality?

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* Presented at the Urbana Meeting of the A.S C., April 19, 1916.

In 1911—that is, at the time when the author became interested in this field—in New York City alone there were at least twenty firms engaged in the composition-flooring business, and the competition was very keen indeed. All of the companies were cutting prices in order to secure business, and many of the firms were putting down the cheapest mixtures which they could conceive. In fact, everything possible was being done to minimise the cost of the product, without much regard for the requirements of a correctly made mixture. The components of the mixtures were weighed and mixed by ordinary labourers, so that it was quite impossible for the mixtures to be of a definite consistent composition. Consequently, all of the manufacturers were experiencing decided trouble with their floors. To illustrate, the colour frequently "went bad;" some floors would crack or bulge, and at no time could they be assured of a satisfactory floor. As a result many floors had to be relaid. Then, too, the cost of magnesite was constantly increasing, labour costs were high, and the selling price was so low that it was impossible to make a reasonable profit out of the business.

At the time of this investigation the red mixture in use by the donors of the Hydrolith Fellowship was supposed to contain—

Ingredients.	Percentages.
Magnesite	50
Sawdust	9
Red colour	10
Clay	11
Terra alba	10
Infusoria earth	10

Some very good floors were made from this composition, and again some could not have been worse. In some cases the floors expanded, while in other cases they contracted and cracked badly. Then in certain of the floors the colour faded decidedly, so that in a short time the appearance became very unattractive.

Experimental.

The investigation conducted by the author at the Mellon Institute of Industrial Research included overcoming the change in colour, obviating the expansion and contraction, and reducing the cost in any legitimate way.

The first experiments carried out were for the determination of the correct amount of magnesite and magnesium chloride to be used, the effect of different fillers, and the results of working samples in various ways. Red coloured mixtures were used in this series, which consisted of 1000 samples. All of the materials entering into the compositions were carefully weighed, made up into 500-g. samples, and thoroughly mixed before the addition of the magnesium chloride solution, the strength and amount of which were also very accurately determined.

The result of this series of experiments showed that with the fillers employed it was necessary to have present not less than 8 or 9 per cent of magnesium chloride and from 20 to 30 per cent of commercial magnesia. When an extremely hard and durable flooring composition was desired, still larger amounts were required. In samples where more than 1 part of magnesium chloride was employed to 3 parts of magnesia, there was always a tendency for the excess of magnesium chloride to come to the surface.

In a number of experiments terra alba was the only filler employed with the exception of sawdust; in others infusorial earth was used, while in still others clay was the only filler besides sawdust. These tests were carried out in parallel, *i.e.*, each day samples were made containing the same percentage of magnesium chloride and magnesite with the same percentage of each of the different fillers. This was done for the purpose of studying the relative effect of each filler and to ascertain whether all acted in the same manner. The only noticeable differences were in the samples in which clay and infusorial earth were employed. Since these substances are lighter than terra alba, it was found that the samples covered more space than those in which terra alba alone was used. It was also learned that, on account of the greater bulk of these substances, they hardened more slowly and invariably gave less hard samples than those in which terra alba alone was employed. The terra alba samples hardened first, those containing infusorial earth next, and the ones with clay last. Clay quite appreciably retarded the settling of the cement.

Determinations were made of the least amount of colour which could be used to obtain the desired shade. Varying amounts of Venetian red were employed, and it was ascertained that 10 to 12 per cent were necessary. Determinations were also made of the greatest amount of sawdust which could be used to obtain a floor which would not be liable to expand or contract and would yet be of sufficient hardness. It was found that samples containing 6 to 8 per cent of sawdust were very hard and did not impart the proper resistance or elasticity to the floor; but that samples with 10 to 12 per cent, according to the other fillers used, were very satisfactory. Samples containing a higher percentage of sawdust hardened very slowly, and those with from 16 to 20 per cent of this material were always quite soft after drying. It was found, however, that this large amount of sawdust could be used with advantage in the under fibrous coat.

Following the completion of this preliminary work, the author superintended the laying of a floor of 550 sq. ft., following the formula which had given the best results in the laboratory experiments, the composition being—

Ingredients.	Percentages.
Magnesium chloride	10
Magnesia	40
Sawdust	10
Red colour	12
Clay	20
Terra alba	8

The materials were carefully weighed and thoroughly mixed, the dry mixture was then incorporated with the calculated amount of magnesium chloride solution, and water was added until the proper consistency was attained. The mixing was continued until all lumps had disappeared and the mixture was then applied over metallic laths. It hardened slowly, but when hard it gave a perfect floor which exhibited no physical changes after the expiration of six months.

A second series of experiments was taken up in order to determine the effect of different fillers upon the hardness, colour, and surface of the floor and the effect of various combinations of fillers. It was thought that such an investigation would supply information which would enable one to select the materials giving best results, and that if there was no difference in the results obtained by the employment of various fillers, the cheapest thereof could be selected.

It was found that in samples containing small percentages of magnesium chloride and oxide the hardening occurred much more slowly than when a greater percentage of the actual cementing material was used. In samples containing high percentages of terra alba, infusorial earth, or clay, the difference in the time of setting was quite noticeable; without exception, the samples containing terra alba hardened first, those containing infusorial earth next, and those filled with clay last. In samples with higher percentages of cement this difference was not so pronounced, but still it could be observed. In all experiments wherein these ingredients were added as the only mineral filler, the terra alba samples were hardest, and there was little, if any, difference between the clay and the infusorial earth samples. It is, of course, a question as to whether this hardness will cause a floor to wear longer than a floor with more resilience which gives rather than wears. If, however, such hardness is desirable it can be attained by using greater percentages of cement with the clay and infusorial earth. In none of the samples could any apparent objection be found to any of the fillers in reference to their effect on the surface. All samples, whether containing but one filler or all three, appeared to give the same finish. It was found, however, that when the samples contained a large percentage of clay or infusorial earth it was necessary to use more colour.

Regarding the amount of magnesite and magnesium chloride necessary the results of this series of experiments showed clearly that never more than 40 per cent of magnesite or 12 per cent of magnesium chloride could be employed. In tests where more than these percentages were used a very hard floor was obtained, whereas the smaller amount gave a sufficiently hard composition. The only samples in this series of experiments which showed a tendency to develop physical defects were those which contained high percentages of magnesite and magnesium chloride. In every case where the percentage of magnesium chloride was more than one-third that of the magnesite there was a tendency for the excess chloride to come to the surface.

In a third series of experiments an effort was made to study the relation of the mass of composition to the volume of magnesium chloride solution sufficient to make a mixture of the proper consistency for laying. This was considered important, since, in preparing the mixture, the workmen invariably used a sufficient amount of magnesium chloride solution of a certain degree Baumé regardless of the actual magnesium chloride contained therein. For example, it was customary to use a 21° Bé. solution in summer and an 18° Bé. solution in winter. Accordingly, solutions of these strengths were used in the experiments. The solid constituents of the mixture were made up to 250 g., and to these samples enough magnesium chloride solution was added to obtain the proper consistency for laying. From the amount of solution required, the actual weight of the magnesium chloride used was calculated, and from this the percentage of magnesium chloride in the finished product was computed.

The average amount of magnesium chloride solution required for 32 samples of this composition was 178 cc. with a maximum of 225 cc. and a minimum of 160 cc. The average amount of magnesium chloride added in per cent was 11·1 for the 18° Bé. solution and 13·3 for the 21° Bé. solution. The maximum percentage required for the 18° Bé. solution was 13·8 and the minimum 10·2. It was found that mixtures containing a large amount of clay or sawdust required enough of the magnesium chloride solution in mixing to bring the percentage of magnesium chloride above the 1 : 3 limit; in such samples it was found that there was always a tendency of the floor to warp on standing.

These experiments demonstrated that in order to obtain the best results the strength of the magnesium chloride solution should be known, and just sufficient of it should be added to secure the correct percentage of magnesium chloride with enough additional water to obtain the proper consistency.

In connection with the third series of experiments, slate was used as the colouring material, but it was found to give very uncertain results. Talc was also tried as a filler, and it was found that when used in moderate amounts it aided greatly in giving the floor a lustre when properly trowelled; moreover, the tests showed that it slightly decreased the absorption of the material. When too much talc is used, however, it constantly comes to the surface, especially after the sample is washed and allowed to dry slowly. Some experiments which were made to determine the largest amount of sawdust that could be used showed that the greatest that could be safely and successfully employed was 15 per cent. In these samples it was necessary not to have an excess of magnesium chloride, for bad warping occurred when too much was used. Sand was also experimented with as a filler and it was found that a very hard composition resulted with a large percentage of sand. While it is difficult to obtain sand of such fineness as to permit of the production of a very smooth surface, it aids in producing a hard durable floor.

The results of ten other experimental series may be briefly noted. Efforts to find a substitute for Venetian red established the fact that while hematite of desired colour would cost, when using 25 per cent of colour, at least two-thirds as much as Venetian red, the colour obtained was one that did not meet with general approval and twice as much was required to produce the same colour intensity as that imparted by the prepared colour. In connection with reducing the cost of the colour about 30 samples were made in which aniline dyes were used; none of these retained their colour for any length of time.

In one series in which varying amounts of sawdust and asbestos were used, it was found that when used in too great quantities, asbestos interfered somewhat with the trowelling; the results obtained indicated that not more than 5 per cent of asbestos should be employed, since greater amounts interfered with the production of a good surface.

A series of experiments was carried out for the purpose of studying the effect of adding oil to the composition and then comparing the absorption of samples made from different fillers. The samples were all made on the same day, and an attempt was made to trowel each sample in the same manner. In the samples in which oil was used the oil was thoroughly mixed therewith, and then these samples were brought to the proper consistency by the use of a calculated amount of concentrated magnesium chloride solution and water. The samples were allowed to stand one week, and then a part of each sample was used for an absorption test. The samples were weighed, immersed in water for twenty-four hours, and reweighed. These samples were then placed aside for four months, weighed, immersed in water, and then reweighed. The absorption was not proportional to the amount of oil used, but after the samples had stood for some time they all absorbed more water, with the exception of those in which linseed oil was used. These showed no indication of oil on the surface, while those in which hard mineral oil was used possessed an oily appearance. The results indicated that the magnesium linoleate acted as a binder between the particles, thus lowering the absorption. The samples in which a small amount of oil was used were sufficiently hard; but when a large amount of oil was employed several months of standing were necessary for the samples to become satisfactory in this respect. The samples without oil faded badly after the absorption test, while little change could be observed in the colour of the samples which contained oil. Invariably the samples containing oil set more slowly.

Experiments were conducted with the object of reducing the cost of the composition by employing other materials with reduced amounts of magnesite. Portland cement-magnesite mixtures had a bad colour, absorbed a large amount of water, and shrank on drying; in general, they resembled more closely the cement than the composition floors. Plaster of Paris gave compositions which dusted badly, lacked hardness, and set too quickly. Likewise, gypsum which had been heated to 400° C. gave samples which set too quickly and were no harder than the samples made from ordinary plaster of Paris. Samples prepared with the addition of a cement made of molecular quantities of magnesia, magnesium sulphate, and plaster of Paris, said to form a white, quick setting strong cement, also set quite quickly and were very hard, but the material rubbed off easily.

In the effort to find the material which would be a suitable binder for fillers or one that could well be used as a surface material, a number of experiments were made with asphalt, "Redmanite," gelatin-glycerol mixtures, "Galalith," viscose, and vegetable resins. No results of commercial importance were obtained.

Finally, it may be mentioned that in 1912 a section of a floor, 12 ft. by 16 ft., was laid in a factory room which was in constant use; this floor was put down in the centre of the room and was subjected to a great deal of wear. It was scrubbed every day with alkaline cleansing material and hot water. At the end of seven months the floor was reported to be entirely set and as good as terrazo. Further experience warranted the conclusion that the flooring, the composition of which was identical with that laid in 1911, noted above, was more desirable than a floor constructed from a hard non-pliable, highly conductive substance like terrazo.

Practical Conclusions.

The successful working of composition flooring of the type considered does not depend entirely upon the chemical composition, but also upon the mechanical manipulation. The exercise of constant care is necessary in laying the floor and consequently only skilled workmen should be employed in practice; in particular, composition flooring should not be over-trowelled, and the necessary precautions should always be taken in laying floors over surfaces which are subjected to heat. The composition should be dependent upon the uses to which the floor is to be put; but a formula is given which, when suitably modified along the lines indicated and expertly used, will comply with the conditions usually encountered in practice.

(This report presents the results of a part of the work done during the author's tenure of the "Hydrolith Fellowship"—September 21, 1911, to March 1, 1913—Industrial Fellowship No. 8, at the Melton Institute of Industrial Research of the University of Pittsburgh. The investigation was carried out under the direction of Dr. Raymond F. Bacon).—*Journal of Industrial and Engineering Chemistry*, viii., No. 8.

ANNUAL REPORT OF THE INTERNATIONAL COMMITTEE ON ATOMIC WEIGHTS, 1917.*

The following new determinations of atomic weights have been published since the issue of the last Annual Report:—

Hydrogen.—Burt and Edgar (*Phil. Trans.*, 1916, ccxvi., 393) conclude from a long series of experiments that the ratio of the combining volumes of hydrogen and oxygen is represented with a high degree of probability by the figure 2·00288 at 0° and 760 mm. pressure. Assuming Morley's values for the densities of hydrogen and oxygen, namely, 0·089873 and 1·42900 respectively, the atomic weight of hydrogen is found to be 1·00772. This new value for H is very nearly the arithmetic mean of the independent values obtained by Morley and Noyes. It may be taken, therefore, that the true value for H lies very close to 1·0077.

Zinc.—Baxter and Grose (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 868), by the electrolysis of zinc bromide, find Zn = 65·388.

Cadmium.—Baxter, Grose, and Hartmann (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 857), by the electrolysis of cadmium bromide, find Cd = 112·407. Similar analyses of the chloride gave Cd = 112·413. Œchsner de Coninck and Gérard (*Comptes Rendus*, 1915, clxi., 676), by reducing cadmium carbonate to metal, found Cd = 112·32.

International Atomic Weights. (1917).

	Symbol.	Atomic weight
Aluminium	Al	27·1
Antimony	Sb	120·2
Argon	A	39·88
Arsenic	As	74·96
Barium	Ba	137·37
Bismuth	Bi	208·0
Boron	B	11·0
Bromine	Br	79·92
Cadmium	Cd	112·40
Cæsium	Cs	132·81
Calcium	Ca	40·07
Carbon	C	12·005
Cerium	Ce	140·25
Chlorine	Cl	35·46
Chromium	Cr	52·0
Cobalt	Co	58·97
Columbium	Cb	93·1
Copper	Cu	63·57
Dysprosium	Dy	162·5
Erbium	Er	167·7
Europium	Eu	152·0
Fluorine	F	19·0
Gadolinium	Gd	157·3
Gallium	Ga	69·9
Germanium	Ge	72·5
Glucinum	Gl	9·1
Gold	Au	197·2
Helium	He	4·00
Holmium	Ho	163·5
Hydrogen	H	1·008
Indium	In	114·8
Iodine	I	126·92
Iridium	Ir	193·1
Iron	Fe	55·84
Krypton	Kr	82·92
Lanthanum	La	139·0
Lead	Pb	207·20
Lithium	Li	6·94
Lutecium	Lu	175·0
Magnesium	Mg	24·32
Manganese	Mn	54·93
Mercury	Hg	200·6
Molybdenum	Mo	96·0
Neodymium	Nd	144·3
Neon	Ne	20·2
Nickel	Ni	58·68
Niton (radium emanation)	Nt	222·4
Nitrogen	N	14·01
Osmium	Os	190·9
Oxygen	O	16·00
Palladium	Pd	106·7
Phosphorus	P	31·04
Platinum	Pt	195·2
Potassium	K	39·10
Praseodymium	Pr	140·9
Radium	Ra	226·0
Rhodium	Rh	102·9
Rubidium	Rb	85·45
Ruthenium	Ru	101·7
Samarium	Sa	150·4
Scandium	Sc	44·1
Selenium	Se	79·2
Silicon	Si	28·3
Silver	Ag	107·88
Sodium	Na	23·00
Strontium	Sr	87·63
Sulphur	S	32·06
Tantalum	Ta	181·5
Tellurium	Te	127·5
Terbium	Tb	159·2
Thallium	Tl	204·0
Thorium	Th	232·4
Thulium	Tm	168·5
Tin	Sn	118·7

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* From the *Journal of the American Chemical Society*, xxxviii., No. 11.

	Symbol.	Atomic weight.
Titanium	Ti	48·1
Tungsten	W	184·0
Uranium	U	238·2
Vanadium	V	51·0
Xenon	Xe	130·2
Ytterbium (Neoytterbium)	Yb	173·5
Yttrium	Yt	88·7
Zinc	Zn	65·37
Zirconium	Zr	90·6

Lead.—Hönigschmid and Horovitz (*Monatsh.*, 1915, xxxvi., 355), by analyses of the chloride, found for common lead the value $\mathrm{Pb} = 207{\cdot}180$. Similar analyses of radioactive lead chloride from various sources gave atomic weight values ranging from 206·050 to 206·084.

Bismuth.—Œchsner de Coninck and Gérard (*Comptes Rendus*, 1916, clxii., 252), by reduction of bismuth chloride to metal, found $\mathrm{Bi} = 208{\cdot}50$).

Molybdenum.—Müller (*Journ. Am. Chem. Soc.*, 1915, xxxvii., 2046), by oxidation of the metal, found $\mathrm{Mo} = 96{\cdot}035$.

Neodymium.—Baxter, Whitcomb, Stewart, and Chapin (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 302), by analyses of the chloride, find $\mathrm{Nd} = 144{\cdot}27$.

Columbium.—Smith and Van Haagen (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 1783), from the ratio between sodium columbate ($NaCbO_3$) and sodium chloride, find $\mathrm{Cb} = 93{\cdot}13$. The value 93·1 might be adopted in the table.

Argon.—Schultze (*Ann. Phys.*, 1915, [4], xlviii., 269) has re-determined the density of argon. The corresponding atomic weight is $\mathrm{A} = 39{\cdot}945$.

(Signed) F. W. Clarke,
T. E. Thorpe,
G. Urbain.

Note.—Because of the European war the Committee has had much difficulty in the way of correspondence. The German member, Prof. Ostwald, has not been heard from in connection with this report. Possibly the censorship of letters, either in Germany or *en route*, has led to a miscarriage.—F. W. Clarke, Chairman.

EMPIRE TRADE NOTES.*

Little Trade Things that Matter.

Not enough is still being done to impress the popular imagination with the extent to which we are freeing ourselves from Germany's pre-war economic domination. Government departments and leaders of industry have, it is true, issued statements or made speeches dealing with big trades such as the manufacture of palm-kernel oil or key industries like dyes or specialised products such as optical glass, and pointed out how, after the war, we shall be well on the way to supplying all our own demands for these products. But these statements, interesting and gratifying as they are, leave the man in the street rather cold, and his wife, who must by no means be left out of account, even colder. It is through the small things of life that the average being is best touched. Take advertised proprietary articles. A certain very popular household cleaning preparation was for some time after the start of the war most difficult—often impossible—to obtain. Inquiries as to the cause of this from the average grocer brought the reply that the essential part of this preparation was derived from powdering a stone which could only be got in Germany. It has now been found that a certain waste product from the Cornish mines is just as effective for the particular purpose as the German stone, and the cleaning preparation, so made, is again freely obtainable. But—and here is the point—while the German source of the raw material before the war has received such a tremendous advertisement, the fact that an equally effective British source has been discovered and is now being used has received no advertisement at all. The same sort of thing has, the British Empire Producers' Organisation understands, happened with regard to various other proprietary articles in everyday use. There is, of course, a difficulty in the way of the manufacturers of proprietary articles disclosing the exact composition of their products, but effective and intelligent advertising should surely have brought out the main facts in this case—which in themselves constitute a fine "selling proposition"—somehow.

A Precious Empire Asset.

The discovery of large and valuable deposits of bauxite (from which ore is extracted aluminium) in the Demerara River District, British Guiana, has caused an influx of applications for permission to explore Crown Lands in that Colony for further deposits. The British Empire Producers' Organisation learns, however, that with the exceptions of the leases to one company, negotiations for which were almost concluded before the outbreak of war, no titles for exploring or mining bauxite have been issued, and none is likely to be issued till after the war. The whole question of the granting of these exploitation licences is, in view of the commercial and military value of aluminium, of great Imperial importance, and the Imperial authorities have rightly decided that the handling of what may prove a great Imperial asset requires careful consideration. At the same time, there seems no reason why that consideration should be indefinitely deferred, and why, under proper sefeguards to retain the control of this asset for the Empire, exploitation of the deposits forthwith should not be encouraged. The war may yet last a long time, and it will scarcely be possible to hold up all trade and development questions till peace arrives.

Rice as a Vegetable.

The importance of the annual rice crop to Burma is again manifested by the returns for the year ended June 30th last, which are just to hand from India. This year production has increased, the total estimated output of unhusked rice amounting to 6,913,000 tons, as against 6,657,000 tons for the previous year. A great deal of this will be eaten in Burma itself, but the forecast estimate of the surplus available for export is 2,700,000 tons, and this forecast is supported by the final crop figures. The difficulty in the present state of transport will be to get this crop away to the consumer. For the purchases made on behalf of the British Empire and its Allies freight will presumably be provided, and the extent to which such freight is available will probably be the only limit to the demand. The British Empire Producers' Organisation believes that after the war rice is destined to come into far greater consumption in the United Kingdom than hitherto. Before the war, for instance, the use of rice as a vegetable in this country was almost entirely confined to those who had lived in the tropics. During the last three years, however, its food value has been increasingly recognised here, a fact which its authorised introduction into war bread has served to emphasise.

Less Cotton from Egypt.

It is most unfortunate that at the exact moment when a further output of Empire-grown cotton is urgently needed, the production of Egyptian cotton should have to be curtailed and wheat substituted. It is unfortunate, but it seems inevitable. Except where the cotton area has been largely restricted, Egypt has never been able to grow enough cereals to meet her own wants. She is now faced with the necessity of growing more wheat to meet the larger local consumption due to the increased military forces in the country, and to replace the restricted imports due to lack of tonnage. It is presumed by the British Empire Producers' Organisation that the whole question was thoroughly considered before the Government came to the present decision, which is naturally a serious one. Egyptian cotton, and more of it, is badly wanted in Manchester, but the food question in Egypt must, of course, be paramount.

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* Published Monthly by the British Empire Producers' Organisation, Kingsway House, Kingsway, London.

West Indies' Food Shortage.

In certain of the British West Indian islands lack of tonnage for the import of foodstuffs has already necessitated some increase in the local cultivation of such products, but hitherto, as far as the British Empire Producers' Organisation is aware, this has been done up till now without prejudice to the local staple export crops—such as sugar. The threatened withdrawal for war service of the subsidised steamship service between Canada and the West Indies would have meant a heavy reduction in the import to certain British West Indian islands of Canadian wheat, but the prompt representation of the Canadian Government (which pays the subsidy) averted such a calamity. Under the irresistible pressure of the war, however, the danger may recur, and though the case of the West Indies is by no means on all fours with that of Egypt, the production of a larger amount of foodstuffs in such of those colonies as have the land and labour available would be a desirable form of food insurance, if nothing more.

Chewing Gum.

The British Empire Producers' Organisation points out that chicle, or sapodilla gum, an important product of British Honduras, is the principal ingredient of chewing gum, the use of which in this country is now widespread, chiefly amongst our soldiers, but also amongst the workers of South Wales, Lancashire and Yorkshire, Glasgow, and London. This Empire product- chicle—has been for many years past exported from British Honduras exclusively to the United States, where the chewing gum habit is an old one. During the last year or two Canada has imported chicle and manufactured gum. Thus the chewing gum now being used in this country comes mainly from the United States, and to a less extent from Canada. But there is no reason why chicle, the sole application of which is in the preparation of chewing gum, should not be imported direct to this country and manufactured here both for home use and for export. That the gum habit is spreading abroad is shown by the exports from the United States, which have risen from a value of £1114 in 1910 to well over £200,000 during the past twelve months. Here is a chance of starting a new manufacture in this country, with a good home market assured and a prospect of a profitable export trade as well.

NOTICES OF BOOKS.

A Class-book of Organic Chemistry. By J. B. Cohen, Ph.D., B.Sc., F.R.S. London: Macmillan and Co., Ltd. 1917. Pp. viii+344. Price 4s. 6d.

This book contains a full first year's course of work in organic chemistry, and serves the double purpose of a theoretical text-book and laboratory guide. The general principles of organic chemistry are first discussed, ethyl and methyl alcohols being treated in considerable detail to illustrate these principles and their application. It is undoubtedly worth while to spend a comparatively long time over this preliminary work, and the thorough grounding given in Prof. Cohen's book will provide a valuable foundation for future study. Part II. is devoted to the aliphatic and Part III. to the aromatic compounds, which are treated somewhat more shortly. A set of general questions and problems completes the book, which is well adapted for use in the higher classes of schools as well as for first year college students. Clear and adequate directions for performing nearly 200 experiments are given, and at the end of each chapter there is a collection of good searching questions, to answer which will often demand both careful thought and a fair amount of knowledge.

Scientific Treatise on Smoke Abatement. By H. Hamilton, A.R.San.I., A.M.I.Mech.E. Manchester: Sherratt and Hughes. 1917. Pp. xiii+155. Price 5s. net.

This book is intended for the use of students who are hoping to take the examination of the Royal Sanitary Institute, and also for practical men, engineers, manufacturers, &c. In the endeavour to avoid being too technical the author has omitted a detailed treatment of chemistry of fuels and combustion, and such discussion of the subject as is included is necessarily rather sketchy and unsatisfactory from the scientific point of view, although, perhaps, adequate for the needs of the practical man. Different types of furnaces, mechanical stokers, &c., are fully described and illustrated, and some account is given of the tests applied to various types of domestic fire-grate by the Coal Smoke Abatement Society. The law relating to smoke production is outlined, and a very brief account is given of the application of gas, oil, and electricity for heating.

Soap. By William H. Simmons, B.Sc. (Lond.), F.C.S. London, Bath, New York, and Melbourne: Sir Isaac Pitman and Sons, Ltd. Pp. ix+124. Price 2s. net.

This book belongs to a series on common commodities of commerce, in which are included books giving general information on a number of natural and artificial products, such as sugar, wheat, rubber, coal, leather, &c. The chief users of the series will probably be teachers and students of geography and technology and manufacturers, and the requirements of both have been well kept in view. Although a certain amount of scientific knowledge would be necessary to understand thoroughly the text of this book on soap, technicalities are avoided in it very successfully, and a subject of considerable interest is treated in such a way that the general public would be quite likely to find entertainment as well as instruction in the text. The different raw materials of the soap making industry are first considered in turn, and full and up to date information is given about the common fats and fatty oils, the alkalis, potash and soda compounds, and the more important essential oils and perfumes used in soaps. The methods employed in soap making are then described, and the characteristics of the different classes of soaps are fully explained. Finally, the properties and action of soap and the principles of its commercial valuation are discussed, and a short account of the manufacture and properties of glycerin brings to an end a useful little work.

CORRESPONDENCE.

WHOLE WHEAT FLOUR.

To the Editor of the Chemical News.

Sir,—The following statements may be of interest to your readers, and it would be an easy matter for scientists to decide if they are correct.

1. Whole wheat is a perfect natural food, containing all the elements required by the human body in a similar proportion to cow's milk, the value of which in health-building is well known.

2. White flour contains approximately 75 per cent of the bulk of the wheat, therefore we waste 25 per cent, this waste containing about 75 per cent of the mineral salts of the wheat as well as valuable aids to digestion.

3. White flour is not a complete food, whereas whole wheat flour is. Mice fed on white flour only will die in about a month, but if fed on whole meal they thrive and grow healthy.

4. A commission set up in the United States to investigate the causes of a certain bone disease in the Southern States found that it was caused by the high proportion of white flour bread being used as food by the poorer classes, and it was remedied by the use of whole wheat meal, which they found contained certain aids to digestion.

If the above statements are correct then it is the duty of some one who has the power to see that we do not go on wasting 25 per cent of our wheat and at the same time using a flour that is useless as a food by itself.

My reason for writing is that if the above is only approximately correct then by adopting whole meal flour we are going to increase the effectiveness of our wheat supply by 33 per cent, which you will admit is a step in the right direction.

Adopt whole wheat flour and the health of the nation will improve by leaps and bounds, but let our scientists and doctors prove it by practical experiments on human beings. I don't know whether my statements are correct or not, for I collected them from various books.

I apologise for trespassing on your valuable space, but think that if there is any truth in the above then under the present crisis it is of national importance.—I am, &c.,

Robt. A. Adams.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxv., No. 7, August 13; No. 8, August 20, 1917.

These numbers contain no chemical matter.

No. 9, August 27, 1917.

Different Modes of Decomposition of Amines by Catalysis; Return of Substituted Anilines to Aniline.—Paul Sabatier and G. Gaudion.—When amines are subjected to the action of finely-divided nickel at temperatures above 300° hydrogen may be removed without affecting the amine function, or a nitrile may be formed, or cyclisation may occur. On the other hand, ammonia may be separated or a molecule of amine less complex than the primitive amine. Thus from methyl or ethylaniline aniline may be obtained.

Bulletin de la Société Chimique de France.
Vol. xxi.-xxii., No. 7, 1917.

Determination of Succinic Acid.—Egerton Charles Grey.—Pasteur's method of separating succinic acid from other acids produced by fermentation was based on treating the salts of calcium with a mixture of ether and ethyl alcohol. Calcium succinate is insoluble, and the other salts of calcium in the mixture are soluble. This method is, however, liable to errors, the causes of which are as follows:—The solvent action of ethyl alcohol on calcium succinate, the presence of substances which prevent the crystallisation of calcium succinate, the presence of a trace of acid in the alcohol employed, and losses during the washing of the precipitate and the concentration of the liquid. If the author's directions are exactly followed these errors can be avoided. All the acids are first determined by means of calcium, and then the quantity of calcium which remains in the alcoholic solution after the precipitation of succinate of lime.

MISCELLANEOUS.

Direct Method for the Estimation of Starch.—T. von Fellenberg (*Mitt. Lebensmitteluntens. Hyg.*, 1916, vii., 369; through *Chem. Zentr.*, 1917, i., 450).—In the method described the starch is dissolved in calcium chloride solution, then precipitated by hydrogen; the iodine-starch compound is decomposed with alcohol, and the starch is weighed. A quantity of from 0·3 to 1·0 grm. of the fat-free substance in which the starch is to be estimated is moistened with water, 20 cc. of 50 per cent calcium chloride solution are added, the mixture is heated in a boiling water-bath for thirty minutes, then boiled for five minutes, cooled, diluted to 100 cc., and filtered through cotton-wool and asbestos. It is sometimes necessary to submit the filtrate to centrifugal action in order to obtain a perfectly clear liquid. Fifty cc. of the filtrate are now treated with N/50 iodine solution until a flocculent precipitate forms, the addition of a large excess of iodine being avoided. After twenty-four hours a quantity of asbestos-wool is added, the precipitate and asbestos are collected in a Gooch crucible containing a layer of asbestos, and the mixture in the crucible is washed four times with 5 per cent calcium chloride solution containing a few drops of iodine solution. The contents of the crucible are then extracted thoroughly with 85 per cent alcohol, and finally with 100 cc. of 90 per cent alcohol. If this treatment does not render the precipitate colourless a quantity of hot alcohol is added to the crucible. After further washing with cold alcohol 5 per cent calcium chloride solution, and dry ether, the crucible and its contents are dried, weighed, ignited, and re-weighed. The loss in weight gives the quantity of starch present.—*The Analyst*, xlii., No. 497.

The Faraday Society.—A General Discussion on "Pyrometers and Pyrometry" will be held on Wednesday, November 7, 1917, at 8 p.m., in the Rooms of the Royal Society of Arts, John Street, Adelphi, London, W.C. 2. The following is the programme:—

Sir Robert Hadfield, Bart., F.R.S., President of the Society, will preside over the Discussion and deliver an Introductory Address.

Dr. E. F. Northrup (Trenton, N.J.) will send in a communication entitled, "High Temperature Production and its Measurement."

Dr. Ezer Griffiths and Mr. F. H. Schofield, B.A., B.Sc. (National Physical Laboratory), will read a paper on "Pyrometer Standardisation."

Mr. R. S. Whipple (Cambridge) will read a paper on "The Advantage of Burying the Cold Junction of a Thermo-couple as a means of Maintaining it at a Constant Temperature."

Mr. Richard P. Brown (Philadelphia) will read a paper and give a demonstration on "The Automatic Control Measurement of High Temperatures."

Prof. J. O. Arnold, F.R.S. (Sheffield), will speak on "Pyrometry Applied to the Hardening of High Speed Steel."

Mr. Cosmo Johns (Sheffield) will speak on "Determining the Temperature of Liquid Metals by means of Optical Pyrometers."

Dr. W. H. Hatfield (Sheffield) will read a paper on "Pyrometry from the Standpoint of Ferrous Metallurgy."

Mr. H. Watkin (Stoke-on-Trent) will read a paper on "The Measurement of High Temperature by means of Pottery Materials."

Mr. C. R. Darling will read a paper on "Base-metal Thermo-electric Pyrometers."

Dr. J. W. Mellor, Mr. F. Twyman, and Mr. G. E. M. Stone will also contribute to the discussion.

Instruments will be exhibited by Mr. Richard P. Brown, the Cambridge Scientific Instrument Company, Messrs. Hadfields, Ltd., Mr. H. L. Heathcote, Mr. Robert W. Paul, Messrs. Siemens Bros. and Co., Ltd.

THE CHEMICAL NEWS

VOL. CXVI, NO. 3022.

CHEMISTRY AND THE NATION.*

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THE unhappy events of the last three years have brought the science of chemistry very much before the public eye. Although the appreciation of the national importance of chemistry by the scientifically trained mind remains as it was before the war, every issue of a daily newspaper indicates clearly that the general public, the public authorities, and our governing bodies now regard as vital to the interests of the country a science which they previously left unconsidered as being of purely academic interest.

This reversal of public opinion is but one of many revolutionary changes which have occurred within a very short space of time. War is a calamity the terror of which no adjective can suitably emphasise but it has proved a more intensive educational agent than could have been foreseen. Thus it is now seriously contemplated that primary and secondary school teachers shall, in the future, command enhanced consideration as exercising some influence on the welfare of the state; if this novel view is put into action you school teachers will be called upon to accept far more responsibility in shaping the educational policy and the destinies of the nation than has been hitherto the case. These altered prospects make it desirable that you should carefully inform yourselves upon the causes and nature of the changes which are proceeding in public opinion with reference to scientific subjects in which you do not necessarily possess the knowledge of a specialist.

For this reason such a series of lectures as this which Sir Robert Blair and his colleagues have organised can be productive of nothing but good, and every student of science honoured by the opportunity of addressing you must welcome the occasion of laying before you facts and considerations concerning his own subject.

Let us commence by enquiring why chemistry has so suddenly loomed large before the public eye. Three years ago an imperative demand arose for supplies of explosives in unprecedentedly large quantities. The explosives mainly concerned were cordite for propellant purposes, and for trinitrotoluene, picric acid, and ammonium nitrate for use as high explosive or shell bursting charges; these in addition to a number of allied products in smaller quantities.

The manufacture of these materials necessitates an ample provision of nitric and sulphuric acids, of cotton, of glycerin (produced during the manufacture of soap), of toluene and benzene (separated from coal-tar), of phenol (extracted from coal-tar or manufactured synthetically from coal-tar benzene), and of ammonia (produced from gas-liquor). In each of these primary requirements the chemical industries of the British Isles were found deplorably lacking, the available output representing but a small fraction of the demand. Our nitric acid has to be prepared from Chili saltpetre, our sulphuric acid from Spanish pyrites, and our production of phenol and toluene was small because pre-war industries in which these materials are used were not flourishing in this country. It will be noted that we are dependent in a large measure for these raw materials upon imports from over-sea States, and that this is in itself a serious factor in determining the present high cost of the ordinary essentials of life. Furthermore, our country was to a great extent unprovided with the works and equipment by which these raw materials are converted into finished explosives.

The extent of the deficiency can be best realised by reflecting upon the enormous magnitude to which our Department of Explosives Supplies has grown since its initiation shortly after the outbreak of war. This Department has amply overtaken our deficiencies in connection with the supply of explosives, although naturally at a very inflated cost.

This single example of a gigantic emergency expenditure upon a purely chemical industry makes it easy to discern one reason why the public and the politician have so suddenly become imbued with a quite embarrassing respect for chemical science; the appreciation which a thoroughly ignorant person expresses towards any particular object is generally directly proportional to the financial outlay incurred.

Our disadvantageous position in connection with the manufacture of explosives is, however, but one result of our comparative isolation from the great chemical manufacturing centres of the world. Large quantities of many essential pharmaceutical products were not made within our Empire, but were exported to us from Germany; the production of these substances as an emergency measure in Great Britain has led to much activity during the last few years in the manufacture of fine chemicals. Certain raw materials required in agriculture and in medicine, such as potash and bromine, were only obtainable from Germany, and our shortage in these essentials has not yet been made up. Just as much importance attaches to the lack of ample supplies of important pharmaceutical and agricultural requisites as to the shortage of explosives supplies, although disaster is not so immediately imminent in the former as in the latter case.

Let us now review the position which prevailed in Central Europe with regard to explosives supplies before the war. Germany held almost the whole of the coal-tar colour trade of the world; this means that she had, immediately mobilisable, the raw materials, works, equipment, and personnel, for the manufacture of almost limitless quantities of explosives. The same industry served her for the manufacture of the great bulk of the more costly pharmaceutical and photographic chemicals sold throughout the world at a splendid profit. Sulphur, to feed her ample sulphuric acid plants, she drew from home resources or from adjacent countries; nitric acid and ammonia she had learnt to make from atmospheric nitrogen, and toluene and phenol she drew from her gigantic coal-tar industry in quantities which undoubtedly satisfied any reasonable prophet as to possible war requirements. The only other requirements for explosive supplies are glycerin and cotton, and of these a shortage probably exists; we have heard much of the lack of fats, the raw material for the manufacture of glycerin, in Germany, and cotton is probably not absolutely essential to the preparation of propellant explosives for military purposes. We have, however, only recently placed restrictions on the entrance of cotton into Central Europe.

From what has been said it will be seen that Germany prepared for war by the establishment of a huge fine chemical industry, built up about the coal-tar colour manufacture, whilst by exporting a large proportion of the world's requirements of dye-stuffs and pharmaceutical and photographic chemicals she acquired a very profitable foreign trade, and prevented her future enemies from preparing for eventual hostilities. This was done in face of the fact that our country was once the greatest producers of rough chemicals, such as sulphuric and nitric acids, and has always possessed a flourishing heavy chemical industry, and the fact that the coal-tar colour industry was established in this country before it ultimately found a more favourable environment in Germany. So completely had we lost the coal-tar colour industry that until a few years ago this country sent coal-tar to Germany and received finished coal-tar colours in exchange; previous to 1914, however, Germany had become entirely independent of our supplies, and produced at home all the crude coal-tar products needed for her colour industry.

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* A Lecture to Teachers given at the Regent Street Polytechnic on Saturday, October 6, 1917, under the auspices of the London County Council Education Department.

This particular instance, showing the manner in which the fine organic chemical industry of the world has been largely absorbed by Germany, greatly to her financial profit in peace and to her potential advantage in war, is only one of the many striking cases which have been long appreciated by the student of chemistry. The fact that so large a proportion of the Australian metallic ores were shipped to Germany to be worked up into products saleable at a high profit, that the monazite sands of Southern India were sent to Germany to be ultimately exported in the form of very valuable incandescent gas mantles, that the thermos flask, invented by a distinguished British chemist, was not manufactured here, but was exploited with large profits in Germany. These and innumerable other instances in which we have exhibited no interest in scientific chemical invention, but have left our present enemies to reap a rich financial harvest are notorious. It must, however, be noted that Great Britain has had the first refusal of all these splendid developments of scientific investigation; we initiated the coal-tar colour industry, the Australian metal deposits and the Indian monazite sands are ours, the thermos flask was invented here. We may go further than this and note that Great Britain possesses immense resources in bromine in the residues obtained in the separation of salt from sea-water in India, that the dynamo was invented in England, and that not long ago our country manufactured textile fabrics for all the world, and saw no prospects of success for any competing nation.

However, matters of this kind are no longer known only to small groups of specialists, but have by sheer stress of the present struggle for existence, become perceived—perhaps dimly, but still perceived—by the thinking mass of our countrymen.

We must ask ourselves first, why these things were not generally perceived before; and, secondly, how we may profit by our experience of the last three years.

Practically every useful chemical development of a technical kind has arisen as the result of some purely scientific investigation. The first coal-tar colour was made by Perkin whilst he was occupied with the artificial preparation of quinine, the incandescent gas mantle was produced by Auer during a purely scientific study of certain rare earths, and the thermos flask was constructed by Dewar for the then technically uninteresting purpose of conserving liquefied gases; the list might be extended indefinitely. In our country a knowledge and an appreciation of scientific discoveries was at one time fashionable; the Royal Institution, in which Sir Humphry Davy, Michael Faraday, and John Tyndall did practically the whole of their work, was established and partially endowed as an expression of this transient mode of thought. But this epoch has passed away, and for decades past pure science has been little appreciated and pure research little encouraged in Great Britain. The Government valuation of pure scientific research has been represented by a grant of £4000 per annum given to the Royal Society for many years past for expenditure on scientific research, and of this a part has been earmarked for purposes somewhat incongruous in kind.

The fruits of the work of the men just named, and of others perhaps only less eminent as purely scientific investigators, have, in the hands of practical men of affairs, brought untold wealth to this country; they would suffice to pay our present national debt many times over. The practical men of mid Victorian days understood this, and acquitted themselves valiantly in establishing the great engineering and chemical industries in this country; but they were succeeded by others of less virility, who started not where their fathers left off, but where they began. Disraeli's dictum, that the practical man is one who perpetuates the errors of his predecessors, was untrue before his day but has been amply justified during the past forty years. For many years past there has certainly been increased disinclination on the part of business and administrative people in Great Britain to recognise and encourage scientific research as the fount of all material progress.

No greater condemnation of the system under which we have been living for decades past, that of allowing our purely scientific activities to languish for lack of funds and to be exploited abroad for the profit of some foreign community, can be imagined than is provided by the recent establishment of the Department for Scientific and Industrial Research with a Government endowment of £1,000,000 for expenditure on original scientific investigation. It would be interesting to have a candid answer to the question why this expenditure was not incurred twenty years ago, when it would have been undoubtedly successful in preventing the horrors of the last three years.

This is, of course, no time for recrimination concerning past errors, but it is to be noted that the establishment of such a research organisation, with such an endowment, indicates that science and the community at large, as represented by the Government, are for the first time agreed that the loss of our technical industries is mainly due to a previous neglect of the vital importance of purely scientific research to the major interests of the nation.

We are thus to a certain extent clear as to the way in which we have allowed so many important technical industries to leave our shores, accompanied by the raw materials necessary to their nutrition. The scientific foundations of these industries were in most cases laid in this country, but the manufacturing interest left us, or never became firmly established with us, by reason of the total disregard of science by both our governing and our governed classes. It cannot be said that scientific men have failed to give warning of what was taking place; during the last thirty or forty years Roscoe, Meldola, Armstrong, and many others of like eminence have loudly predicted calamity as the inevitable result of such neglect of chemical science. In this, as in many other respects, we have suffered as a nation from the exclusively British plan of making the specialist subservient to the administrator, the latter being chosen because he is available, politically acceptable, and because he knows nothing whatever about the subject which is to be administered, and is therefore not likely to be prejudiced by any previous convictions. That process of appointing someone who knows nothing to supervise the work of someone who does know how to do the job seems to have been at the bottom of a great many of our misfortunes in the past. Even in 1915 the Government applied this method of appointing administrators possessing no scientific or technical knowledge with a mandate to re-establish the coal-tar colour industry in this country; naturally enough, the Government organisation for this purpose has proved so far a failure, and has, indeed, retarded the object for which it was instituted.

This kind of benevolent but mistaken activity arises from lack of education; people who have too little breadth of knowledge and outlook to enable them to realise the difficulties attendant upon any particular situation are apt to enter lightly upon an enterprise which others, understanding better, would handle with some sense of responsibility. If it were generally demanded that no person should be regarded as decently educated who had not mastered the rudimentary principles of natural science, such a farce as has been created by the national effort to re-establish the coal-tar colour industry in Great Britain could not have been staged for the amusement of the whole world. This demand is one that can be made by the teachers, and, with the possession of wider powers for counsel and execution, the responsibility for making it will fall upon you.

We may hope to profit by past mistakes through realising how they occurred; but it has still to be seen how we are to ensure that the earlier situation, which arose from contempt of scientific effort, does not become re-established at some later date. One obvious danger lies in the fact that those administrators who were previously the most apathetic to every scientific or educational interest are now the most vociferous in its promotion; we have yet to be convinced as to the sincerity of these sudden conversions, and in any case a sustained breeze of public opinion will assist in keeping the weathercock pointing in the direction of progress.

Abundant evidence is available to prove that the great modern developments of industrial chemistry, which have contributed so greatly to the amenities of life, have all arisen as the result of pure scientific research. This work has often been initiated and carried out by men of entirely academic instincts. Faraday, from whose early chemical investigations every form of electric motor has been developed, and Perkin, who initiated the coal-tar industry, were both unattracted by commercial problems. The former, despite the enormous stimulus which he gave to many scientific industries, spent his later years in receipt of a civil list pension; the latter did indeed apply himself for a number of years to developing the colour industry, but so soon as the opportunity offered abandoned technical work and spent the rest of life in pure chemical research in a field far removed from industrial interests. On the other hand, Weldon and Mond, the chief founders of the great heavy industry of Great Britain, spent their whole lives in the development of chemical technology, although again upon the basis of purely scientific investigations carried out in the laboratory.

Thus all progress in industrial chemistry in the past has originated in the scientific laboratory, and it is safe to predict that in the future, when advance will depend more than ever upon delicate laboratory research, scientific investigation is bound to command even more attention as the fountain head of technical progress.

The first great demand which our country must make, if the finer chemical industries are to find a congenial soil in these islands, is for the training of large numbers of selected students in the methods and aims of chemical research. Amongst our young men is always found a certain proportion attracted by temperament and by talent towards the natural sciences. One particular type of personality occurs very frequently among our countrymen—a type endowed with a high order of intelligence, a large measure of manipulative dexterity, and a keen desire to peer a little further than has been seen before into the mysteries of the universe. These are the men who should be assisted by every possible means to enter an obviously appropriate career in one of the natural sciences. Hitherto students of this particular type have been "combed out" in a manner highly pernicious to the interests both of the nation and of themselves. Their intelligence and their aptitude for assimilating knowledge has led the classical teacher to press upon them the advantages of a classical career. The law, again, absorbs a large proportion of the young men of the nation who are best fitted for a scientific career; this is a question of such gravity as to demand the most careful attention.

If our country is to cope successfully with the huge constructive problems which are now being thrust upon it, some method must be devised for preventing the reckless waste of intelligence and ability upon quite unworthy objects which now goes on. It must be recognised that the possession of talents carries with it a duty towards national interests as well as a potentiality for acquiring personal wealth. The young man of the type capable of advancing knowledge, who is potentially able to complete a fruitful career by leaving the world the richer for his having lived, should not be tempted into such a "blind alley" occupation as that of the bar, with the ultimate prospect of quitting the world having made no contribution to its progress. Nothing is more saddening than to read the reminiscences of some great legal luminary, a man almost always endowed with exquisite intellectual powers and of immense virility, to note the delight which the writer displays in each miserable piece of legal chicanery in which his own wits have been pitted against others of similar brilliance, and to realise that this splendid personality has passed from among us leaving nothing for which mankind can call him blessed. Other instances will occur to you in illustration of that reckless squandering of creative talent which has been one of Britain's besetting sins for a century past.

The task of directing the young mind into some appropriate road of future activity should fall directly upon the teacher. I incline to the belief that this honourable burden has been too lightly regarded in the past, but as increase of status inevitably brings increase of responsibility, scientific men will look much more to the schools in the future for assistance in the recruitment of scientific talent.

It is somewhat surprising that primary and secondary school teachers have not contributed more to the advancement of science; the teacher possesses more than average ability, generally has the rudiments of a liberal scientific education, and is certainly not deficient in perseverance.

Many years ago I held the post of head of the Chemistry Department in one of the London Polytechnics, and had to deal with large numbers of school teachers who were desirous of learning chemistry for such purposes as the Board of Education or the University of London examinations. Naturally I was myself keenly interested in original chemical research, and I soon found that many of my students evinced a very pronounced taste for the same kind of work. During the few years which I spent at the Goldsmiths' Institute quite a number of elementary school teachers devoted their evenings to chemical investigation, and much of the work which was thus done took its place as a real contribution to our knowledge of organic chemistry. I am sure that the work done by these old friends of mine has proved a very lasting source of satisfaction to them. I know that other institutions in London have been able to draw upon this great reservoir of latent scientific talent in the same way, but everyone would welcome an extension of the principle involved. One of the foremost geologists of the day started his career as an elementary school teacher, and there seems no reason why the profession of a primary teacher should not in many more cases lead to the higher positions in science.

Perhaps I have digressed considerably from the subject laid down in the title of this present address. But one of the great problems which has to be faced in the near future is the provision of men and women capable of initiating and executing that exact work which is the basis of all scientific knowledge and scientific industry; and this is a matter in which you teachers are just as much interested as the scientific man is and as the nation should be.

I have also wandered into discussing natural science as a whole, instead of inviting your attention solely to the national importance of chemistry. This, however, was inevitable. We have seen that chemistry looms large in the public vision at the present crucial juncture because our corporate existence has been found suddenly to depend upon the immediate development of the chemical resources of the Empire to an extent previously inconceivable; but this concentration of attention upon one branch of science is accidental, and is, indeed, liable to mischievous misapprehension. The lesson to be learnt from the last three years trial is, not that the cultivation of chemistry alone is an imperative necessity, but that every effort is needed for the stimulation of all branches of natural science throughout our empire; no sacrifice of brains, time, or money must be thought too great with this prime object in view. The free and unfettered development of one branch of natural knowledge must go hand in hand with similar progress in all others. Let us consider one very striking example.

The development of the relation between chemistry on the one hand and pathology and physiology on the other is at present in its infancy. Every chemist who has devoted himself to studying the bearings of his science upon medicine and surgery, and every pathologist who has interested himself in the chemical aspects of his subject, has reaped a rich reward. The surgeon Simpson introduced the chemical agent chloroform for anæsthetic purposes; the pathologist Jenner imagined an entirely novel chemical conception which resulted in the practical abolition of smallpox; and yet another, Lister, introduced the purely chemical idea of the antiseptic treatment of wounds. The chemist Pasteur devised a mode of treatment which has practically eradicated hydrophobia from Europe. The continuation of this partnership between chemistry and pathology has led to the elimination of many of the horrors formerly attaching to typhoid, tetanus, diphtheria, and even syphilis. The absorption into medicine, surgery, and public health of some of the fundamental facts and conclusions of chemistry has, in fact, led to the doubling of the average length of human life.

Each step in the wonderful development of this one small branch of scientific knowledge has been effected by one man, and at a very small cost in brains and treasure; each step has added fabulous wealth to the world's resources.

Is it possible to doubt that the endowment on a large scale of chemico-therapeutic research on diseases which have hitherto resisted treatment, either partially or wholly—diseases such as phthisis and cancer—would lead to the discovery of entirely efficient methods for combating these scourges of our race? When one reflects that chemical pathology has at quite negligible cost provided almost certain methods for the prevention or cure of diseases previously regarded as highly fatal, it is difficult to see why the nation does not give the chemical pathologist unlimited financial support in his attempt to investigate and eliminate less understood but equally devastating maladies. Much public and private financial support has, of course, already been forthcoming for this and similar objects, and with very fruitful results; but the whole point is that the scale upon which operations have proceeded is far too small in view of the importance of the object in view. The expenditure of a few million pounds on the chemico-therapeutic study of phthisis and cancer would certainly lead to vast improvements in our methods of dealing with these plagues.

The chief conclusions which I would ask you to draw from what I have said to-day, and from much more which time has not permitted me to say, but which is available to the student of scientific and national history, are the following. It is essential that public opinion should become sufficiently educated to understand that concentration upon scientific progress is not only urgent in time of war, but that it is vital in time of peace. That we cannot afford to spare any effort which the nation can make in the enlistment of its best young intelligence in the service of science, and that for this reason some means should be devised for putting an end to the squandering of intelligence upon unworthy objects. That all should realise that scientific progress is synonymous with national progress.

To grasp these conclusions, and to apply them in dealing with the young, is one of the major duties which has to be allotted to our school teachers.

FUMIGATION AS A DISINFECTING AGENCY.

By C. T. KINGZETT, F.I.C., F.C.S.,
H. F. BOTTOMLEY, F.C.S., and J. E. BRIMLEY, B.Sc.

In a leading medical journal published in the United States of America (*Boston Medical and Surgical Journal*, March 9, 1916) will be found an account of certain experiments made by Dr. W. W. Walcott (State District Health Officer of Massachusetts), in conjunction with Dr. Curtis, from which it was concluded that fumigation is useless for the purpose of disinfection; but as this conclusion was directly opposed to our views based upon previous experimental work of our own and others, we resolved to make the subject one of further exact investigation. For this purpose a chamber of 1018 cubic feet capacity, made of brickwork, lined internally with white porcelain tiles (so that it could be easily washed and cleansed), was specially constructed, having one window opening from the outside (in order to allow the gaseous contents to escape at the end of each experiment), and two doors forming a lobby entrance, so that the apartment could be easily entered and thoroughly sealed.

Immediately before the testings a twenty-four hours' broth culture of *B. Typhosus* of good strain was absorbed by strips of sterilised filter-paper (1 inch by ½ inch), and these moist unwrapped strips were placed in open Petri dishes in several parts of the chamber—(*a*) on the floor, (*b*) on a table 4 feet above the floor, and (*c*) on the top of a compartment 6 ft. 4 in. high. Other strips similarly soaked were done up in fine muslin, 9 inches by 3 inches, wrapped round three times (so that they were wholly enclosed), and laid on open Petri dishes in the same situations. They were then exposed to various fumigations, as will be described, and at the conclusion of each experiment transferred to sterilised broth contained in tubes and incubated for at least seventy-two hours at 37° C. All the growths, where any, gave the characteristic appearance of *B. Typhosus*.

Many series of experiments made over the last fifteen months have been conducted and repeated at different times of the year, using fumigations of:—

1. Formaldehyde, as generated by the volatilisation of paraform in the form of tablets, and using tha direct heat of a wax night-light.
2. Formaldehyde, as generated by the evaporation of a 40 per cent solution of that liquid, using the direct heat of a wax night-light.
3. Formaldehyde, as generated by the action of permanganate of potassium upon a 40 per cent solution of formaldehyde.
4. Mixed vapours of sulphur dioxide and formaldehyde, as generated by several appliances in which the burning sulphur was made to generate the formaldehyde vapour from solid paraform and 40 per cent liquid formaldehyde respectively.
5. Vapour of sulphur dioxide, as generated from burning sulphur candles.
6. Sulphur dioxide vapour, generated as in 5, but in association with aqueous vapour, the burning sulphur being utilised to vaporise the water contained in a surrounding jacket.

The results so obtained varied within certain limitations with the special construction of the several appliances used, and to some extent doubtless with the temperature of the fumigating chamber and the humidity of the air; but they were, all the same, very definite and precise in character, and may be summarised as follows:—

First, as regards paraform and formaldehyde vapours, it may be said that no matter how generated, similar quantities were found to exercise the same destructive action, and it was ascertained that this action was neither accelerated nor increased by association with aqueous vapour.

No advantage whatever was presented by the employment of formaldehyde solution as compared with dry paraform, and, on the other hand, a slight disadvantage was experienced by the use of the permanganate method, as this necessarily causes the chemical destruction of a portion of the formaldehyde itself.

The use of 20 grms. of paraform, or an equivalent amount of formaldehyde liquid—that is, 1¾ ozs. of the 40 per cent solution—invariably destroyed the unwrapped and wrapped cultures within a period of two hours in a space of 1018 cubic feet. 17 grms. of paraform was the actual *minimum* quantity found to be effective.

With the permanganate appliance it was found necessary to use 2 ozs. of the 40 per cent formaldehyde and ¾ oz.

of the permanganate as a minimum to effect the disinfection within the two hours' period.

As to the mixed vapours of sulphur dioxide and formaldehyde; it made no difference whether paraform or 40 per cent solution of formaldehyde was used as the source of the formaldehyde vapour, and it was found that with the special apparatus which we employed, complete disinfection was effected within two hours of both the unwrapped and wrapped cultures, using either—

(1) $2\frac{3}{4}$ ozs. sulphur and 11 grms. of paraform, or
(2) $2\frac{1}{2}$ ozs. sulphur and $11\frac{1}{2}$ grms. formaldehyde as generated from 1 fl. oz. of the 40 per cent solution.

A great number of experiments had to be made before these—the best results—were obtained. As already noted, they were found to depend to some extent upon the temperature of the atmosphere and its humidity, and more considerably upon the particular construction of the apparatus, which, in its most effective form, was designed to burn the sulphur as quickly as possible, and to generate in this way sufficient heat to cause the thorough vaporisation of the formaldehyde.

It is obvious from the results that the combination of the two gases (sulphur dioxide and formaldehyde vapour) presents, or may present, advantages in certain cases, namely, those in which there are more highly-developed organisms in addition to bacteria which it may be desirable to destroy at the same time, such as moths, fleas, and bugs.

With sulphur candles the use of water-vapour as generated simultaneously with the sulphur dioxide, proved, as was to be expected from our previous experiments, very helpful, and it was found necessary to use as a minimum 9 ozs. of sulphur in association with 6 ozs. of water to secure thorough disinfection within two hoors of both the unwrapped and wrapped cultures. Without the joint use of water-vapour, as much as 16 ozs. of sulphur was required as the minimum, and a longer period of exposure (five to six hours).

Here, again, of course, the results were variable to some extent, being largely dependent upon the particular construction of the apparatus; but the recorded results were the best actually and repeatedly obtained at different times of the year and at atmospheric temperatures ranging from 38° to 80° F. It should be noted that in many cases it was found that the unwrapped cultures were destroyed some time before the wrapped ones. In practice, however, it proved desirable to work upon a two hours' exposure standard, and the results have been standardised upon that basis. In all cases there were control cultures, and in every case these were found to be actively alive after seventy-two hours.

It is not difficult to understand how Dr. Walcott and his associate arrived at their conclusions, as in their experience whenever they found that fumigation had destroyed the germs with which they experimented, the control cultures were also found to be dead. It may be observed that instead of making use of laboratory cultures, "because of the possibility of their being attenuated," they used as their materials "smears and swabs from noses, throats, and ears," from contagious wards and from "suppurating wounds." Why, then, it may be asked, were the control cultures found to be dead after certain exposures without fumigation? We entertain no doubt that the "smears and swabs" were too insignificant in amount, and that consequently desiccation, causing starvation, destroyed the germs in all cases. Moreover, such materials should not be employed, bearing in mind that disinfection of this sort is in no way concerned with infected persons, but only with infectious material, of which they are the source; and, as was pointed out by Dr. Kenwood many years ago—("The Disinfection of Rooms," by Henry Kenwood, M.B., D.Ph.; a paper read at a Congress of the Sanitary Institute, held at Leeds, 1897)—in ordinary practice we probably have to deal with non-spore-bearing bacteria and of comparatively easy destructibility, and these bacteria do not find at their site of lodgment anything approaching the fostering and protective properties of the nutrient media, in which they are planted in experiments. It is interesting also to note that Dr. Kenwood reported at the same time that the evidence furnished by a population of over a quarter of a million had proved that sulphur dioxide disinfection of rooms very rarely breaks down in practice.

On another occasion—(In the discussion of a paper read at the Bristol Medical Assoc., Edinburgh, July 29, 1898, by Dr. F. J. Allan and Cecil H. Cribb, B.Sc., F.I.C.)—he reported that while he had found ten paraform tablets to each 1000 cubic feet of space unreliable, it was necessary to use about 25 tablets to each 1000 cubic feet to ensure disinfection—an experience in good practical accord with the results of our more recent investigation, which it will be observed has been conducted upon strictly quantitative lines.

We agree with Dr. Kenwood that in respect of the ordinary infectious diseases, the infections to be dealt with are easily destroyed under the circumstances of their existence apart from the human body, nor have we any hesitation in concluding that fumigation with formaldehyde or sulphur dioxide, as described in our experiments, secures absolutely effectual disinfection to the extent that is sought by Medical Officers of Health in dealing with rooms that have been occupied by infectious cases.

Our investigation establishes the non-necessity of employing complicated apparatus for the generation of formaldehyde vapour under pressure, and the equal efficacy of paraform, which can be used with more convenience in practice. It also as clearly re-establishes the efficacy of disinfection with sulphur dioxide gas, particularly when generated in association with aqueous vapour.

(The several appliances as used by the authors can be obtained from the Sanitas Co., Ltd., Limehouse, London, E. 14).—*Medical Press and Circular*, August 29, 1917.

THE MOLECULAR WEIGHTS OF THE TRIARYLMETHYLS.

By M. GOMBERG and C. S. SCHOEPFLE,
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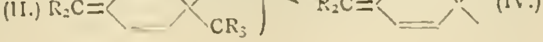
It is now generally accepted that the free radicles of the triphenylmethane series owe their unique unsaturated character to the presence of a trivalent carbon atom in the molecule. In many cases the molecular weight has been found to be double that calculated for the free radical. Nevertheless, even in these cases the presence of a compound with a single unsaturated carbon atom is still recognised, and the assumption is made that there exists, in virtue of partial dissociation, a mobile equilibrium :—

$$R_3C—CR_3 \rightleftharpoons R_3C + R_3C.$$

It is doubtful whether the matter is quite as simple as it is represented by the above equation. From a variety of experimental evidence the conclusion seems inevitable that both the hexa-arylethanes and the triarylmethyls exists in two tautomeric modifications (Gomberg, *Ber.*, 1907, xl., 1860; 1909, xlii., 406; Gomberg and Cone, *Liebig's Ann.*, 1909, ccclxx., 190; 1910, ccclxxvi., 208). It is far more likely that triarylmethyls, at least when in solution, conform to the following scheme (Gomberg, *Ber.*, 1913, xlvi., 406) :—



In other words, there is a tautomeric equilibrium between the benzenoid hexa-arylethane (I.) and the quinol (II.); also between the benzenoid triarylmethyl (III.) wherein the central carbon atom is trivalent and its quinonoid modification (IV.), wherein the *para*-carbon atom in the nucleus assumes the trivalent state. This viewpoint is in entire harmony with the peculiar chemical and physical behaviour of this class of compounds. It permits us to explain, by the presence of the quinol tautomer (II.), the existence of a coloured modification of hexa-arylethanes in cases where molecular weight determinations fail to indicate an actually measurable degree of dissociation. And even in those cases where a partial or complete dissociation of the hexa-arylethane is demonstrable, the fact that the solution is coloured finds a more reasonable and more concordant explanation in the existence of the quinonoid tautomeric triarylmethyl (IV.) than merely in that of the benzenoid (III.) alone (compare G. N. Lewis, *Proc. Nat. Acad. Sci.*, 1916, ii., 588).

Whether, however, the supplemental hypothesis of tautomerism is accepted or not, the fact remains that we are dealing primarily with a phenomenon where a hydrocarbon dissociates spontaneously into two parts, which parts may, also spontaneously, reassociate with the production of the original substance. What are the factors which influence the degree of dissociation in a given hexa-arylethane? What is the relation between the degree of the dissociation and the nature of the aryl group in the substituted ethane?

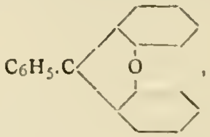
Factors Influencing Dissociation.—Obviously, the nature of the solvent, the temperature of the solution, and the concentration of the solute must be the chief factors as regards the extent of dissociation which may be reached by a given hexa arylethane. With regard to changes in the equilibrium between the dimolecular and the monomolecular modification due to the temperature, it has been found (Gomberg and Cone, *Ber.*, 1904, xxxvii., 2037) that the molecular weight of triphenylmethyl in naphthalene at 79—80° is approximately 414, while the average value found with other solvents, such as benzene, nitrobenzene, &c., which freeze at temperatures around 0—5°, is between 480 and 485. A computation from these molecular weight determinations indicates that triphenylmethyl exists in the monomolecular state to an extent of 17 per cent in naphthalene at 80°, while to considerably less than 5 per cent, if at all, in benzene at 6°. Schlenk and Mair (*Liebig's Ann.*, 1912, cccxciv., 179) determined the molecular weight of triphenylmethyl in benzene by the ebullioscopic method, and found that at the temperature of the boiling-point of benzene, also about 80°, the hydrocarbon is dissociated in the monomolecular phase to the extent of 23·3—29·9 per cent with approximately a 2 per cent concentration. Schmidlin (*Das Triphenylemethyl*, Stuttgart, 1914, 94) calls attention to the fact that it is very difficult to obtain an absolutely pure sample of triphenylmethyl, and that samples prepared by slightly different methods often differ considerably in purity. Therefore he suggests the possibility that the variation between the molecular weights found by Schlenk with the ebullioscopic method, and by Gomberg and Cone with the cryoscopic method may be due to differences in the degree of purity of the samples used. Accordingly, he constructed a special apparatus containing two thermometers, by means of which he could determine the molecular weight in benzene first by the ebullioscopic method and then by the cryoscopic method on one and the same sample. However, the molecular weights of triphenylmethyl found by the two methods showed no appreciable difference in value, and therefore no change in dissociation between the temperatures of 6° and 80° was noticeable.

With regard to the influence of concentration upon the degree of dissociation of hexaphenylethane, an examination of the results obtained by various investigators fails to reveal a concordant influence of this factor. Neither molecular weight determinations nor the application of optical methods have supplied information of a sufficiently decisive nature to warrant us in drawing any conclusion as regards the concentration influences affecting the equilibrium between the dimolecular and the monomolecular triarylmethyl (Piccard, *Liebig's Ann.*, 1911, ccclxxxi., 347).

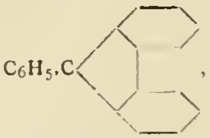
Relation between Dissociation and the Nature of the Aryl Groups.—Although triphenylmethyl, the first and simplest representative of the triarylmethyls, was found to be largely in the dimolecular state, some of its analogues were found to exist to a large extent as monomolecular. Among the first triarylmethyls of this kind was the series containing *p*-biphenyl groups:—

$$(C_6H_5)_2C.(C_6H_4.C_6H_5),\ (C_6H_5)C(C_6H_4.C_6H_5)_2,\ C(C_6H_4\ C_6H_5)_3.$$

Schlenk and his co-workers concluded from the measurements of the molecular weight by the cryoscopic method with benzene as a solvent, that these compounds are monomolecular to the extent of 15, 80, and 100 per cent respectively (Schlenk, *Liebig's Ann.*, 1909, ccclxxii., 4; 1912, cccxciv., 186; *Ber.*, 1910, xliii., 1756; Schmidlin and Garcia Banus, *Ber.*, 1912, xlv., 3176). From these results one might infer that the dissociation of the hexa-arylethane into free radicals is greatly favoured by the complexity or the weight of the aryl groups—the dissociation becoming apparently more manifest also in proportion to the number of such groups. But the hypothesis that the dissociation of the hexa-arylethanes is proportional to the complexity of the aryl groups becomes wholly untenable when one compares triphenylmethyl with phenylxanthyl,—



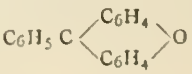
which is monomolecular to the extent of 82 per cent (Schlenk and Renning, *Liebig's Ann.*, 1912, cccxciv., 189). Is the union of the two phenyl groups the paramount influence in this case? If so, why should a substance constitutionally so closely related to the xanthyls as phenyl-biphenylene-methyl,—

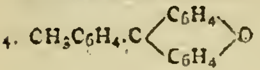


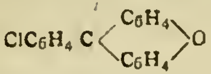
be completely dimolecular? (Schlenk, Herzenstein, and Weickel, *Ber.*, 1910, xliii., 1754).

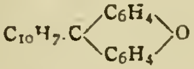
It is obvious that from the few facts known to us at present it is difficult, if not wholly impossible, to formulate the relation between the complexity of the aryl groups in the hexa-arylethanes on the one hand and the tendency of these ethanes toward dissociation into free radicals on the other.

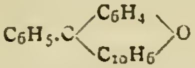
The Problem of this Investigation.—In order to obtain some further knowledge as to the factors governing the equilibrium between the di- and the mono-molecular phases of triarylmethyls, we decided to select for our study a related set of compounds. The following triarylmethyls were prepared for this purpose:—

1. $(C_6H_5)_3C$ .. .. Triphenylmethyl
2. $(C_6H_5)_2C.C_{10}H_7$ .. .. α Naphthyl-diphenylmethyl
3. 
$C_6H_5\,C\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle O$ .. Phenyl-xanthyl

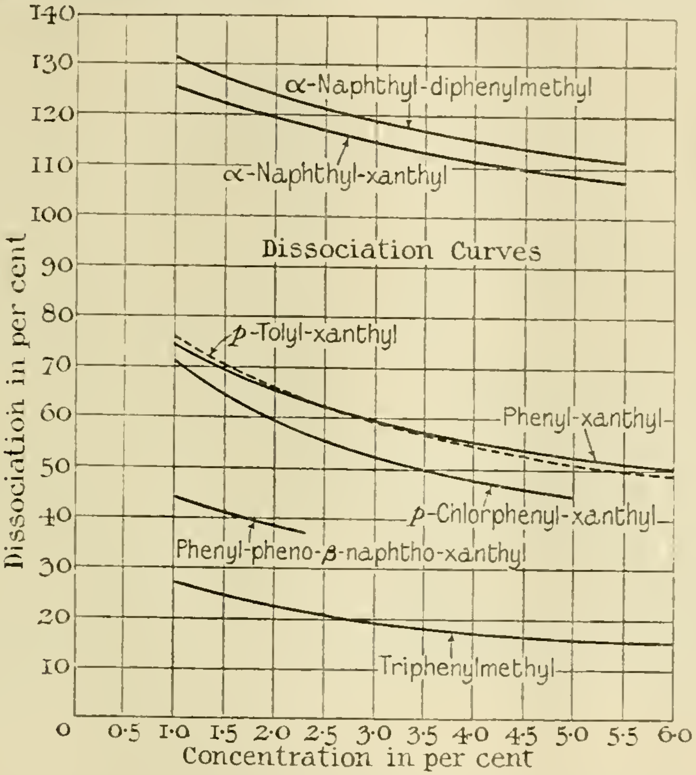
4.  $CH_3C_6H_4.C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}O$. *p*-Tolyl-xanthyl

5.  $ClC_6H_4\,C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}O$ .. *p*-Chlorphenyl-xanthyl

6.  $C_{10}H_7.C{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}O$ .. α Naphthyl-xanthyl

7.  $C_6H_5.C{<}\begin{matrix}C_6H_4\\C_{10}H_6\end{matrix}{>}O$ .. Phenyl-pheno-β naphtho-xanthyl

A determination of the molecular state, and, consequently, of the dissociation phenomenon, of these unsaturated compounds is the more pertinent in view of the limited number of radicals upon which such determinations have been conducted in the past. Further and, if possible, more certain evidence with respect to the dissociation of these hydrocarbons, and, consequently, with respect to the trivalency of carbon, is most desirable.



Our aim has been to take every possible precaution to ensure uniformity and purity of the triarylmethyls to be used. As a check, the capacity for oxygen absorption and for peroxide formation was always resorted to, using part of the very same sample which served for the determination of the molecular weight. This is a very essential and one of the safest criterions for the purity of the products, the reaction being:—

$$2R_3C+O_2=R_3C-O-OR_3-C.$$

Also, it was made certain that during the course of the determination the triarylmethyl suffered no deleterious isomerisation due to the effect of the temperature (80°) of the solvent, naphthalene. Each experiment represents an individual preparation, and in no case were two determinations of the molecular weight made upon the same sample. Moreover, the sample was never more than one day old, the free radical being prepared in the afternoon, allowed to crystallise over-night, isolated the following morning, and the molecular weight taken the same afternoon. The molecular weight determinations themselves were carried out in an atmosphere of hydrogen, oxygen being completely excluded from the whole apparatus. The details regarding the preparation of the pure compounds and the method used in the molecular weight determinations will appear shortly in the *Journal of the American Chemical Society*.

The triarylmethyls were studied from two points of view. 1. The molecular weight of every triarylmethyl was determined within a fairly wide range of concentration, from 1 to 6 per cent, in order to determine the effect of concentration upon the degree of dissociation. 2. From a comparison of the degree of dissociation of various triarylmethyls, under the same conditions of solvent, concentration, and temperature, it was hoped that something would be learned regarding the influence of the various aryl groups upon the tendency of the ethane towards dissociation.

Summary of the Results.—In the diagram are represented the curves, each curve based upon a number of molecular weight determinations, expressing the dissociation tendency of the hexa-arylethanes mentioned in this paper. The curves are plotted with the percentage of concentration as abscissæ and the dissociation values, in percentages, as ordinates. The values expressing dissociation were obtained according to the formula $x = \frac{M_t - M_o}{M_o}$, where x equals the degree of dissociation, M_t represents the theoretical molecular weight of the hexa-arylethane, and M_o the molecular weight actually found.

1. In all instances a steady and gradual increase of the molecular weight is noticeable as one proceeds from a

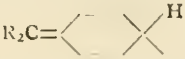
1 per cent concentration of the radical to that of 6 per cent. The generality of these results and their uniformity leave no room for doubt that we are dealing here with a phenomenon of molecular dissociation, wherein the products of dissociation are in equilibrium with the dissociating substance. An equilibrium of this nature might be expected to shift in favour of dissociation with dilution, as is actually the case with these compounds.

2. When in triphenylmethyl two phenyl groups become joined through an oxygen atom, and thus give rise to a xanthone ring, the tendency of the new compound, phenyl xanthyl, towards dissociation increases to a marked extent, approximately threefold.

3. A phenyl and a *p*-tolyl group are apparently equivalent in their influence for dissociation when linked to a xanthone ring; a *p*-chlorphenyl group is of a somewhat lesser influence, as can be seen on comparing the dissociation curves of the three corresponding aryl xanthyls. This equality of influence of a *p*-tolyl and a phenyl group would not necessarily have been anticipated. Tolyldiphenylmethyl differs very much from triphenylmethyl, and tri-*p*-tolylmethyl is so unstable that it is apparently impossible to isolate it owing to the tendency to isomerise or polymerise.

4. An *a*-naphthyl group when replacing a phenyl group in triphenylmethyl exerts upon the dissociation equilibrium of the compound a very decided influence in favour of the monomolecular phase — α-naphthyl-diphenylmethyl appearing as wholly dissociated. This favourable influence of the naphthyl group is still retained when the group is linked to a xanthone ring, the resulting compound being also dissociated to the extent of 100 per cent. And yet, when the naphthyl group enters as a component in the formation of the xanthone ring itself, it depresses very decidedly the dissociation tendency of the compound, as is evident on comparing the two isomers, α-naphthyl-xanthyl and phenyl-pheno-β-naphtho-xanthyl.

5. It has been established that the triarylmethyls are, in the solid state, almost wholly devoid of colour, being, like triphenylmethyl itself, only pale yellow; but their solutions differ very much, being yellow, orange, brown, red, or green, according to the individual compound. Schlenk has described tribiphenylmethyl, 100 per cent dissociated, as a dark green powder. Whether this difference in colour from our completely dissociable radicals is real or only apparent we cannot at present say. The fact that triarylmethyls, colourless when solid, give colour only when in solution, lends support to the hypothesis that the triarylmethyls do undergo tautomerisation when dissolved. Not dissociation alone into triarylmethyl, but, in addition thereto, the consequent tautomerisation of this into its quinonoid modification,—



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constitute a satisfactory explanation of the colour phenomenon. Tautomerisation commonly occurs, indeed, only when the compound capable of tautomerisation is in the liquid phase, or in solution. And that is just the case with the free radicals under consideration.

6. The two radicals, α-naphthyl diphenylmethyl and α-naphthylxanthyl, were found to give a molecular weight *less* than that calculated for the monomolecular phase. Schlenk and Renning's results show that α-naphthyl-biphenyl-phenylmethyl exhibits the same unusual behaviour (*Liebig's Ann.*, 1912, ccccxiv., 195). We have good reasons to believe that our results are not due to experimental errors, and we took pains to verify them repeatedly. The cause of this unexpected result may possibly lie in a still further dissociation of the triarylmethyl itself,—

$$RR'R''C \rightleftharpoons RR'C + R''.$$

—*Proceedings of the National Academy of Sciences*, U.S.A., iii., No. 7.

FUEL RESEARCH.

REPORT OF THE FUEL RESEARCH BOARD ON THEIR SCHEME OF RESEARCH AND ON THE ESTABLISHMENT OF A FUEL RESEARCH STATION.

To the Lord President.

MY LORD,—The Fuel Research Board beg to present to the Committee of the Privy Council for Scientific and Industrial Research the following report on their scheme of research and on the establishment of a fuel research station.

In their first report—(this report was not published)—the Board stated that they had in view two main lines of research. First, a survey and classification of the coal seams in the various mining districts by means of chemical and physical tests in the laboratory, and, second, an investigation of the practical problems which must be solved if any large proportion of the raw coal at present burned in its natural state is to be replaced by the various forms of fuel obtainable from coal by carbonisation and gasification processes.

When the previous report was written it was believed that the survey and classification of coal seams might be proceeded with in advance of the second line of enquiry; but further consideration has shown that from the practical point of view the two lines are so thoroughly interdependent that they can be most satisfactorily dealt with side by side. This view will be further developed after the position and prospects with regard to the second line of enquiry have been more fully explained.

In preparation for the organisation of the first line, however, an experimental study of standard methods for the examination of samples of coal in the laboratory has been made. Hitherto in the systematic examination of coals in the laboratory there has been no generally accepted low-temperature carbonisation test. In the survey and classification of coals for the purposes of the present enquiries a test of this kind is practically indispensable. Certain existing tests are designed to ascertain the suitability of coal for gas or coke making, but as both these methods of carbonisation are carried out at temperatures above 900° C. they give little or no direct information as to the behaviour of the coal when carbonised at 500° to 600° C.

As a result of experimental work carried out for the Board in the Fuel Laboratory of the Imperial College of Science and Technology a test has now been elaborated which by direct weighing and measurement gives the yields of gas, oil, water, and carbonaceous residue which result from carbonisation at any definite temperature. The apparatus is simple and is so arranged that the progress of the distillation can be watched from start to finish. The products can be weighed or measured with reasonable accuracy, and any or all of them can, if desired, be submitted to further examination. The method has been tested on certain typical coals and at a variety of temperatures, but before publishing the results it is proposed to make further tests with a wider range of samples. At the same time steps will be taken to standardise the apparatus and to arrange for its regular production for laboratory use.

With regard to the organisation which will ultimately be required in the principal coal mining districts for the collection and registration of samples the Board are glad to say that they have found every disposition on the part of the representatives of the coal owners to co-operate in this work. It is not proposed to start any extensive organisation for this purpose till the preparations for the second line of enquiry are further advanced. The accumulation of large numbers of samples would serve no useful purpose at present and would be decidedly inconvenient. It is certain that as soon as the arrangements for the examination and testing of samples are in working order it will be an easy matter to maintain the necessary supply of samples to keep the laboratories and the Research Station fully occupied.

In the first report the following statement with regard to the second line of enquiry was made:—

"The second of the proposed lines of enquiry has been led up to by a variety of influences during the past eight or ten years. Among these influences have been, the demands for cheaper and more ample supplies of electrical energy, for home supplies of fuel oil for the Navy, of motor spirit for the Transport and Air Services, and last, though by no means least, for smokeless domestic fuel. This last has been brought about through the growth of public and municipal opinion on the subject of smoke prevention in cities and in industrial centres.

"The only development which would satisfy all these needs simultaneously would be the replacement of a large proportion of the raw coal which is at present burned in boilers, furnaces, and domestic fires, by manufactured fuels prepared from raw coal by submitting it to distillation.

"The greater part of the coal which is consumed in Great Britain is burned in its natural state as it comes from the mines. The question of the moment then is—To what extent can and ought the present use of raw coal to be replaced by the use of one or other of the various forms of fuel manufactured from coal—coke, briquettes, tar, oil, or gas. While there is already in the possession of experts a certain amount of knowledge and experience which might enable them to organise and direct schemes for the replacement of raw coal by manufactured fuel in particular directions and on a fairly large scale, no really comprehensive scheme can be formulated till certain perfectly definite problems in coal distillation have been solved.

"These problems can only be solved by carefully organised experiments on a working scale carried out under the conditions likely to arise in practice."

The gas retort and the coke oven have become highly developed appliances for the carbonisation of coal at temperatures ranging from 900° to 1200° C. In the former the primary object of the carbonisation is to obtain the maximum yield of *gas* suitable for domestic and industrial lighting and heating, while in the latter *coke* is regarded as the principal product. In both cases the by-products of the operation are of economic value, but are necessarily of secondary importance. In considering the broad question of the replacement of any considerable proportion of the coal which is at present being burned in its raw or natural state by manufactured forms of fuel, the part which may be played by high temperature methods of carbonisation will need to be taken into account. For this purpose a great amount of experience is available, and trustworthy data on which to base the calculation of the economic possibilities are in existence.

The distillation of oil shales at low temperatures for the production of mineral oils, paraffin wax, and ammonia is a highly developed industry, but the oil shales are totally unlike coal in their nature and in the products which they yield, so that the experience gained in this industry, though undoubtedly valuable, is only indirectly useful so far as coal is concerned.

As regards the carbonisation of coal at low temperatures there is no corresponding body of experience in existence, and there are very few properly accredited data available. Some work has been done by individual inventors and syndicates, and a certain amount of experience has been gained. While only portions of this experience have been disclosed enough is known to justify the conclusion that much still remains to be done in devising the special forms of apparatus required for the economical carrying out of this type of carbonisation.

The way is clearly open for a serious attempt to determine whether an economical and efficient apparatus can be devised for the carbonisation of coal at low temperatures and whether, by the use of such an apparatus for the carbonisation of properly selected coals, products will be obtained of a collective value greater than that of the original coal plus the cost of carbonisation and handling. Obviously the evolution of an economical and efficient apparatus is at the root of the whole matter, for only after a thoroughly practical apparatus is available can trustworthy tests of the various classes of coal be made and the economic possibilities of the method be fully weighed and considered.

The solution of these fundamental problems will supply a new base from which to attack questions like the following:—

1. Can the 35 to 40 million tons of raw coal which is used every year for domestic heating be wholly or partially replaced by smokeless fuel, solid and gaseous, prepared by the carbonisation of this coal?
2. Can adequate supplies of fuel oil for the Navy be obtained by carbonisation of the coal which is at present used in its raw form for industrial and domestic purposes?
3. Can supplies of town gas be obtained more economically and conveniently by methods of carbonisation and gasification other than those at present in use in gas works?
4. Can electric power be obtained more cheaply if the coal used for steam raising is first subjected to processes of carbonisation and gasification?
5. Will the more scientific development of the preparation and use of fuel, which would be implied in the successful working out of the foregoing questions, enable the peat deposits of the United Kingdom to take a serious place as economic sources of fuel for industrial purposes?
6. Can the use of gaseous fuel in industrial operations be forwarded by the development of more scientific methods of combustion in furnaces, muffles, and ovens used in metallurgical, ceramic, and chemical operations?

The answers to these questions will only be obtained by co-ordinated research carried out on the lines of a broad and well-considered scheme. The subjects to be dealt with are already attracting the attention of serious workers in the industries, and it is to be expected that solutions of some of the problems will be supplied by these workers. The Board sincerely hope that this will be the case. They would regard it as a great misfortune if the establishment of a Government organisation for Fuel Research were to result in the discouragement or limitation in any way of the activities of outside workers or organisations. They venture to hope rather that many of these workers will be disposed to welcome a national scheme of research, the aims of which are broad and yet definite, and in which the more specialised contributions from all sides will naturally take their place.

In considering new and extensive schemes of carbonisation it is necessary to bear in mind that outlets for all the products of carbonisation must be found. The gas, coke, and shale oil industries are all of old standing, and each has had to develop outlets for its products by patient and continuous effort. No new carbonisation scheme can be justified economically if it can only live by poaching on the preserves of the existing industries. Even if an efficient method of low temperature carbonisation is evolved it will be valueless in the wider sense unless profitable outlets for all the important products can be developed. It is obvious that the Fuel Research Board, which is in official touch with the Admiralty, the Ministry of Munitions, the Board of Trade, and other public departments, is exceptionally placed for the furtheranee of schemes which involve the finding of large outlets for products new and old. It is known for instance that the Admiralty attach great importance to the development of supplies of fuel oil from home sources, so that it may be taken for granted that this requirement alone would absorb all the oil which could be produced by the carbonisation of tens of millions of tons of coal per annum. This fact alone gives an entirely new aspect to the extension of carbonisation in hitherto untried directions, but while it will undoubtedly help on the economic side of the problem it in no way relieves the pressure on the technical side. In a way, moreover, it accentuates the problem now to be referred to, the profitable disposal of the coke or carbonaceous residue left when the volatile products are distilled from the coal. The percentage of coke obtained varies with the quality of the coal and the temperature at which it is carbonised, but it may be taken on the average that each ton of coal carbonised will give about 15 cwt. of coke. Thus to obtain one million tons of fuel oil for the Navy it would be necessary to carbonise twenty million tons of coal, and the coke produced would amount to 15 million tons.

The disposal of this very large quantity of coke or char at a profitable price must be regarded as the vital question if low temperature carbonisation is to be established on a sound economic basis. The research scheme must, therefore, include a very complete enquiry on three main lines:—

1. The use and value of this coke for the direct firing of steam boilers.
2. Its gasification in producers for the manufacture of low-grade fuel gas and the recovery of its nitrogen as ammonia,
3. Its use for industrial and domestic heating either directly, as it comes from the retorts or after its conversion into briquettes.

The second of these enquiries will involve the development of a special form of gas producer and auxiliary plant if the best results are to be obtained from the coke. It will also involve the development of a system of boiler firing, in which fuel gas of 130 B.T.U. can be burned at least as efficiently as coal both as regards thermal efficiency and the effective evaporation per square foot of heating surface.

In all that concerns the preparation and use of special forms of fuel there are two distinct stages of development to be successfully passed. In the first stage apparatus and methods have to be evolved and tested till a practical standard of efficiency is reached. In the second stage the consumers of fuel must be induced to study the new appaartus and methods till they thoroughly understand and in the end adopt them. This second stage will be most readily passed, if an expert staff trained at a fuel research station is available to undertake the education of those who desire to adopt the new methods and appliances.

The use of town gas as a fuel for industrial purposes has made great strides during the past few years and a number of experts are to-day engaged on the design and adaptation of furnaces and apparatus for these purposes. The actual practice of gas-heating still lags a long way behind the ideals of economy and efficiency, and there is room for much useful experimental enquiry into principles and methods.

The use of the lower grades of fuel gas though successfully carried out in certain directions is very imperfectly understood in the majority of industries in which gas might be used for heating and power purposes. In this direction there is scope for much useful work both in research and in the education of experts and consumers.

A single illustration may be given of the complicated enquiries which will have to be conducted before an answer can be given to what seems to be a simple question.

There is a very general belief among electrical experts that the future of British industry will be greatly affected by the cost at which power in bulk can be supplied in the form of electricity. It has been proposed, for instance, that large electro-chemical works should be established in this country for the manufacture of products which in the past have been manufactured in parts of the world where cheap water power is available. In this connection it has been suggested that the cost of producing power from coal in this country would be substantially reduced if instead of burning the coal directly under the steam boilers it were first subjected to carbonisation and gasification processes, which in addition to fuel gas would yield valuable by-products. Plausible statements have been issued showing the enormous savings or profits which would accrue if schemes of this sort were adopted. Unfortunately these estimates have generally been made on a very slender foundation of knowledge and experience. On the other hand those who by experience and practice are best qualified to judge, hesitate to prophesy as to what the economic result of a combined carbonisation and power generating scheme would be, but they agree that the interests at stake are so great that the question ought to be authoritatively answered once for all. But no answer can be accepted which is not founded on the complete working out of the scheme, no important step in the series of operations being omitted or slurred over. This series of operations will start from the mechanical preparation of the coal and its conversion into solid, liquid, and gaseous products by carbonisation. It will end with the delivery of a known weight of high pressure steam under the conditions most favourable for power production by turbo-generators. In the proposed scheme of research it will be seen that the investigation of each of the steps involved in the above enquiry is provided for. Three, at least, of these steps involve pioneering work on an industrial scale, and the work may occupy a considerable time. The Board realise that it is possible that the net result of this particular enquiry may be to show that purely as a means of cheapening the cost of electric power, the use of carbonisation methods has not much to commend it, but that certain incidental advantages will justify its use in particular cases.

The Fuel Research Station.

The scheme of research which has been outlined in this Report can only be efficiently carried out in a Fuel Research Station designed and equipped for the purpose in which operations on an industrial scale can be carried out under proper working conditions. The following is a description of the equipment which will be required for the research work at present in view.—

A Railway Siding will pass through or alongside of the station, and the coal to be used in tests will be received in railway waggons at

An Unloading Platform provided with a sampling floor, a coal breaker, and screens, a weighing machine, an elevator, and high-level bunkers, from which the coal will be passed on to

The Retort House.—In this house ample space will be provided for the erection of the various forms of carbonising apparatus which are under investigation. Facilities will be provided for quickly carrying out the necessary changes and improvements in the apparatus as the experimental work proceeds. The hot gases will be led from the Retort House into

The Condenser and Exhauster House, which will be equipped with condensers, washers, scrubbers, exhausters, compressors, meters, pressure regulators, gauges, pumps, motors, and tanks.

For the collection and examination of the gases in bulk *Gas Holders* will be provided.

The hot coke from the Retort House will be elevated to high-level bunkers, from which it can be supplied to gas producers, steam boilers, briquetting plant, or to railway wagons.

The Gas Producer House will be provided with one or more gas producers, with heat exchangers, washers, scrubbers, and liquor tanks.

The Steam Boiler House will be provided with one or more water tube boilers of modern type, and with feed water tanks, water and steam meters, pumps, &c.

The Briquetting House will be provided with grinding, mixing, and briquetting machines.

Tar and Oil Stills and Condensers will be provided for dealing with the liquid products.

The Gas Furnace House will be equipped for the testing of gas muffles, annealing ovens, and melting furnaces.

Laboratories, Offices, and Workshops, suitably equipped, will also be necessary.

As regards the location of this station the desiderata are—That it should be within easy reach of London, that there should be ample railway and other facilities for the transport of coal from all parts of the Kingdom, that there should be ready means for the disposal of the large quantities of coke, oil, and gas which would be produced in the regular course of experimental work, and that a supply of labour, skilled and unskilled, should be available. It was realised that these conditions could only be fulfilled by a site in the neighbourhood of a large gas works, and some months ago the Director of Fuel Research approached Dr. Charles Carpenter on the subject. Dr. Carpenter is Chairman of the South Metropolitan Gas Company, and he is a member of the Carbonisation Sub-Commitee of the Coal Conservation Sub-Committee of the Reconstruction Committee, of which the Director is Vice-Chairman. Following this conference, Dr. Carpenter, on behalf of the Board of the South Metropolitan Gas Company, made the following very generous offer to this Board:—(1) To lease to the Government at a peppercorn rent sufficient land at the East Greenwich Gas Works for the erection of a Research Station, (2) to prepare drawings and specifications for this station on lines to be laid down by this Board, and to make contracts for its erection, (3) to give every facility for the transport of coal and other supplies to the Station and to take over at market prices the surplus products, gas, tar, liquor, and coke resulting from the operations at the Station. After further conferences a suitable site was agreed upon. The proposed site is a strip of level ground about 250 feet wide by 700 to 800 feet long, situated on the main siding which connects the gas works with the South Eastern Railway and with access to an existing road.

The foregoing scheme of research is obviously not intended to cover the whole of the territory which is open for exploration to-day. Still less ought it to be regarded as setting any limits to the exploration of new territories in the future. The root idea of the scheme is that certain fundamental changes in the preparation and use of fuel which have been proposed are of such far-reaching importance that the solution of the technical and economic problems involved ought to take precedence of all other matters. This does not mean that other lines of research will be ignored, but only that the larger issues must be kept well to the front till definite solutions of those technical and economic problems can be given. Though no direct reference has been made to the preparation and use of fuels from Oil Shales, Brown Coals, and Peat, it is obvious that experimental enquiries on these matters will naturally find a place in the developments of the present scheme.

The Research Station, as planned, will be capable of any extensions which will be required for future researches. Out of the four acres which it is proposed to lease for the Station, only one acre will be occupied by buildings under the present scheme. Further, a large part of the equipment of these buildings will be of a permanent character and will serve all the general purposes of a Research Station. Future extensions will, therefore, not repeat this permanent equipment but will be based upon it.

George Beilby, Director of Fuel Research.

September 10, 1917.

Physical Society.—The next meeting will be held at 5 p.m. on Friday, October 26, at the Imperial College of Science, Imperial Institute Road, South Kensington, S.W. The following papers will be read:—"A Class of Multiple Thin Objectives," by T. Smith, B A., and "The Radius of the Electron, and the Nuclear Structure of Atoms," by J. W. Nicholson, F.R.S.

ORDER OF THE MINISTER OF MUNITIONS APPLYING REGULATION 30A TO NITRATE OF SODA.

Ministry of Munitions of War,
Whitehall Place, S.W. 1.
October 18, 1917.

In pursuance of the powers conferred upon him by Regulation 30A of the Defence of the Realm Regulations, the Ministry of Munitions hereby Orders that the war material to which that Regulation applies shall include war material of the following class; that is to say, Nitrate of Soda.

Note.—All applications and communications in connection with the above Order should be addressed to the Department of Explosives Supply, Ministry of Munitions, Storey's Gate, Westminster, S.W. 1.

NOTICES OF BOOKS.

The Theory and Use of Indicators. By E. B. R. Prideaux, M.A., D.Sc. London: Constable and Co., Ltd. 1917. Pp. vii + 375. Price 12s. 6d. net.

The literature of Germany on the theory and use of indicators has been considerably more copious and detailed than our own on the same subject, and hence there is no doubt but that a cordial welcome will await this book, which has drawn upon German treatises and monographs while adding much very valuable new matter. The first chapter deals with physical methods of determining hydrion and hydroxylion concentrations, and electrochemical methods of investigating equilibria are fully described, a good general knowledge of physical chemistry being required of the reader in order that the discussion may be fully appreciated. The text is perhaps a trifle terse, and the chapter is not by any means one which can be quickly read and assimilated. The treatment of light absorption and theories of colour follows, the work of Hantzsch and his co-workers being well explained. A careful study is given of the course of neutralisation and the theory of titration, and finally practical directions are given for testing indicators, with detailed information relating to their chief properties, which will enable the chemist to come to a decision as to the choice of an indicator in different circumstances.

Separation and Identification of Food Colouring Substances. By W. E. Mathewson. Washington: Government Printing Office. 1917. Pp. 56.

In this bulletin issued by the Bureau of Chemistry the author describes a scheme of identification of about 130 dyes or colouring matters commonly found in foods. The methods of separation which have been found to be most suitable for the purpose are explained in full, and tables are given to enable the chemist to extract and rapidly identify the usual colouring matters. Some few tests for natural colouring substances are included, and chemists engaged in food analysis will find the bulletin interesting and useful. Special attention is paid to the reagents necessary for the detection of colouring matters, and the full tables showing the reactions and properties of the 130 dyes will serve to facilitate as far as possible the difficult task of identification.

The Analytical Distillation of Petroleum. By W. F. Rittman and E. W. Dean Washington: Government Printing Office. 1916. Pp. 79. Price 15 cents.

Complaints are frequently made that the reports of different chemists concerning the properties of specimens of petroleum submitted to them for examination differ widely, and there is no doubt but that the establishment of a standard method of distillation would be a great boon both for chemists and refiners. The Bureau of Mines is conducting an investigation for the purpose of working out a satisfactory method, and this report gives the results so far obtained. The best types of apparatus are described, and the Hempel still is mentioned as having marked advantages in the way of cheapness, simplicity, and durability. The phenomenon of cracking was studied in the course of the investigation, and it was found that it is of negligible importance provided that the vapour temperature does not exceed 300° C.

Prospecting and Mining of Copper Ore at Santa Rita, New Mexico. By Donald F. Macdonald and Charles Enzian. Washington: Government Printing Office. 1916. Pp. 122. Price 25 cents.

Modern methods and procedure in mining have given great importance to low grade ores which some years ago were practically valueless, and mining is now to be regarded as a much less speculative industry than it was in the days of estimates of returns based largely upon faith and hope and hardly at all upon careful prospecting and accurate determinations by experts of probable yields and values. In this Bulletin, relating to the establishment and maintenance of the Santa Rita Mining Company's plant, very detailed accounts are given of the organisation of the company and of the processes employed, and assaying methods are fully described with examples of records. The periodical tables compiled in the engineering and accounting departments are shown, and the descriptions of the methods which have been adopted in prospecting and mining the ore will be of considerable value to engineers and managers engaged in like enterprises.

CORRESPONDENCE.

KILN DRYING OF BARLEY.

To the Editor of the Chemical News.

Sir,—With reference to the Memorial from the Vegetarian Federal Union and signed by the President (Mr. Arnold F. Hills), so far as kiln drying of barley is concerned this is a necessary and desirable procedure—necessary because grain harvested with 18 per cent or more of moisture can only be kept when the moisture is reduced to at least 12 per cent, desirable because all barley used for malting purposes has its germinating capacity increased. It seems difficult to believe that, under the circumstances, the vitamines would be impaired.

With regard to the enzyme cellulase, this can only refer to the hemicellulose of the cell walls of the endosperm or the starch grain. There is no enzyme in cereals acting on pure cellulose, such as filter-paper.—I am, &c.,

Chas. E. Franck A.I.C.

OIL OF CLOVES.

To the Editor of the Chemical News.

Sir,—I frequently suffer from nervous toothache or "tic," and find great relief from oil of cloves, but find the smell very objectionable.

Is it possible to remove this odour without interfering with the good properties of the oil? My chemist tells me he does not think it can be done, but I would like to have a higher opinion.

May I trouble you in this matter? Any information through your columns will be much esteemed.—I am, &c.,

W. T. Bell.

EXAMINATIONS IN CHEMISTRY.

To the Editor of the Chemical News.

Sir,—Will any of your readers be so kind as to inform me of any examinations in chemistry (organic or inorganic) which give, on passing them, certificates, so that I may get particulars concerning them.—I am, &c.

T. Mordecai.

MISCELLANEOUS.

An Employer's Duty.—Regulations require employers of labour to make a return of all male employees from sixteen years of age, and on a form (D.R. 17) obtainable at any Post Office, to the Recruiting Officer of the district in which the men work. A duplicate form should be kept by the employer on the premises, and both should be revised monthly if the occasion arises. Failure to comply with this regulation entails heavy penalties under Defence of Realm Regulation 41*a*.

MEETINGS FOR THE WEEK.

Thursday, Nov. 1st.—Royal Society. "Reflexion of Light from a Regularly Stratified Medium," by Lord Rayleigh. "Two Cases of Congenital Night-blindness," by Sir W. Abney. "Duration of Luminosity of Electric Discharge in Gases and Vapours, Further Studies." by Hon. R. J. Strutt. "Surface Reflexion of Earthquake Waves," by G. W. Walker. "Characteristic Frequency and Atomic Number," by H. S Allen.

To comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

Analytical and Metallurgical Chemist seeks Re-enagagement. Sound experience in all Steel and Alloys Analysis and General Assaying. University trained man. Excellent references. Ineligible.—Address, "Metal," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemists, Analytical, two required for Technical Organic Laboratory (Distillation, Fractionation, &c.). Permanency to suitable Men (or Women)—Apply, Manager, British Vegetable Products, Ltd, 1, Chapel Street, Kingston Road, Portsmouth.

Chemist, well up in Oils, Fats, and Organic Chemistry, required for Food Factory in South-West. State age, qualifications, and experience.—Address, "Cathac," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted immediately, Assistant Chemist in Analyst's Laboratory, used to the Analysis of Minerals and Non-ferrous Alloys.—Address, N. F, Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted, in London Laboratory, Lad with some knowledge of Chemistry to train on as Assistant. State education, age, and salary required.—Address, L. W., Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted, RESIN KILN.—Box 383, T. B. Browne's Advertising Offices, 163, Queen Victoria Street London, E.C. 4.

BATTERSEA POLYTECHNIC, LONDON, S.W. 11.

The Governing Body require the services of a TEMPORARY LECTURE ASSISTANT AND LABORATORY STEWARD in the Chemical Department.—Applications, stating education, training, experience, and salary required, should be sent as early as possible to the Secretary.

THE CHEMICAL NEWS

Vol. CXVI., No. 3023

BLOOD CELLS OF HEALTH AND DISEASE.

By SAMPSON MORGAN.

Authorities Quoted. — Huxley, Metchnikoff, Lister, Almroth Wright, Paracelsus, Bacon, Darwin, Henslow, Romanes, Weismann.

In my two previous contributions on "The Rejuvenation of the Earth and Man" and "Can the Human Species be Improved?" I dealt with clean culture from geological and ethical standpoints. I now deal with it from the pathological standpoint.

Are the white corpuscles "pus-cells" indispensables? Prof. Huxley says yes; I say no.

But what is the position of the red corpuscles to the white in the blood of human beings? The same as that of the good bacteria to the bad in soils. There is no difference. The red corpuscles are the corpuscles of cleanness; the white corpuscles of uncleanness. The consumption of inflammatory animal foodstuffs increases the number of the normal white corpuscles and of the "pus-cells," and favours their perpetuation. The consumption of bland vegetable foodstuffs decreases the number of the normal white corpuscles and of the "pus-cells" and hinders their perpetuation.

The greater the preponderance of the red cells the greater the power of the blood to resist infection. The red corpuscles in living beings, and their counterparts in soils, are representatives of health and fruitfulness; the white and their counterparts are the reverse. Bland vegetable foodstuffs alone maintain the red corpuscles at the normal standard, the standard which reduces febrific activity, with its tendency to wear out the human machine before its natural time.

Disease decimates the world, because the standard of the red blood cells is imperfect. The perfect standard can only be reached by the perfect consumption of clean culture grown foodstuffs in great moderation, since this assures the provision of the low nitrogen percentage which I have proved to be the basis of perfect health.

With such food, despite the immoral argument of Herbert Spencer in praise of flesh eating, and the incineration—not burial—of all dead, waste, and effete matters, the "pus-cells" would disappear from the human body, the micro-organisms would find their occupation gone, man would become immune to disease and physically perfect.

The following facts concerning the white corpuscles deserve consideration. Under normal conditions the red blood-cells compared with the white corpuscles occur in great preponderance, the latter representing but a very small fraction of the number of cells in the blood of healthy organisms.

The characteristics of the red blood-cells are totally different to those of the white corpuscles; whilst the red blood-cells in beings of the same kind present great uniformity, the reverse is the case with the white corpuscles. The streams of blood from the liver and spleen are uncommonly rich in white corpuscles. In disease the situation between the red blood-cells and the white corpuscles is completely reversed. The latter then may even attain a numerical preponderance over the former.

B. Coli, the filth feeder and disease carrier, revels in soils fouled by sewage, or to which manure and similar excreta has just been supplied. In a clean virgin sod and soil it is absent, so are all bad organisms. This sod is the sweetest, most healthy, perfect, and productive type of pabulum for all crops conceivable.

Sewage and manure fed to the soil bring huge numbers of putrefactive organisms upon the scene. So improper and bad food, and waste and diseased matter in the human body, provide the ideal conditions for deadly micro-organisms and furnish the perfect material upon which white corpuscles feed and increase amazingly.

The white corpuscle has been denounced as a parasitic animacule, but no proof of this has been forthcoming. Huxley likened it to the amœba met with in stagnant water. This similarity is significant in another way to that inferred by the Professor. It is of the nature of that unclean feeder. It lives in a free state in the blood; the red corpuscle does not. I suggest it is a filth feeder; it lives upon the unclean pabulum in the plasma of the blood, in the same way that the amœba does upon the foul matter in the fetid pond, and bad bacteria upon animal matter and manure in the soil.

The Physical Basis of Life.

In a cleverly written booklet on "The Origin of the World," the author says, "If you look at your own blood under the microscope you will see white corpuscles moving in it. You will recognise in these corpuscles the amœbæ of our first acquaintance, and you will realise that we are of that dim, mysterious, awful past, part of the lowly life that began in the steaming seas of the primitive rocks." And it was this white corpuscle which decreases in the human body in health and increases in the human body in disease, and with greater rapidity as the disease developes in intensity, that the Professor called the physical basis of life, as his *Fortnightly Review* paper shows. He said, except that it is dependent for the conditions of its existence upon the plasma, it might be compared to one of those simple organisms which are met with in stagnant water. Huxley, therefore, did not see that filth was as vital for the presence and existence of the white corpuscle as it was for the amœba.

But I would point out that in the quotation I have given from the great Professor he did not state that the white corpuscle was the amœba but only that it might be compared to it, whereas the author quoted above in error appears to take it for granted that he did.

It is said that "pus-cells" cannot be distinguished at all times from normal leucocytes (white corpuscles) unconnected with inflammatory conditions; the difference is simply one of degree. Those of the putrefactive feeders, which when more unclean and ulcerous matter is formed in or inoculated into the human body leave their blood plasma feeding grounds to feast upon and revel in the more tempting diseased mass (filth) that has newly appeared, are of a more degraded type, partaking of the nature of the new comers.

In these and the preceding remarkable parallels from Nature we have mathematical proof that there is no more place for diseased conditions and bad organisms in a healthy soil than there is for diseased conditions, "pus-cells," and micro-organisms in a healthy body. This is sense and science.

The errors of Huxley in this connection were the errors of the late Prof. Metchnikoff, who said that the white blood cells were beneficent sentinels on guard in the human body, which chased and made war upon harmful bacteria, and, having destroyed, consumed them. This opinion, greeted by the great Lister as "One of the most romantic chapters in the history of medicine," was good matter for a scare paper, but it was not science, as many people have concluded since. That the white corpuscles serve a purpose is true, in the same way that the bad soil bacteria are useful under conditions, that is conditions which should not exist. They are there as filth feeders, because the unhealthy conditions and corrupted waste (filth) are there. With the non-existence of unhealthy conditions and corrupted waste (filth) the red corpuscle, the corpuscle of health, strength, and fruitfulness, alone would rule. So in respect to the soil. The bad organisms are there because of kindred reasons exactly. In a healthy soil, nitrifying organisms, the good bacteria, which in a sweet, well drained aerated soil, thrive freely on uncontaminated green material, moisture, and bland mineral, alone would rule.

I claim that these explanations portray the true character of the white corpuscles, and should prove of considerable usefulness to say the least.

Meat, Manure, and Medicine Unnecessary.

But possibly I can prove my case more effectually by reference to the views of Sir Almroth Wright, the distinguished bacteriologist, who, since the advent of clean culture, agrees that "manures and medicines are unnecessary." But whilst he admits that the fertility of the soil may be maintained without manure, and the health of the body without medicine, and commends my cure for unhealthy conditions in the soil, a clean and natural oneburned earth, yet his cure for unhealthy conditions in the body is an unclean and unnatural one—inoculation with dead animal matter (filth). Why? since there is no difference. We cannot sever the link which binds the vegetable and animal kingdoms.

The inoculators imagine that they can render man immune to disease by the unnatural injection of vaccine (pus) diseased animal matter. But pus is filth, and its introduction into the human body must be attended with awful consequences, as the huge increase in new forms of disease proves. In a perfectly healthy body even normal leucocytes could not thrive. The wise physician, therefore, will seek to eliminate rather than introduce those "pus-cells" of degraded form. This is the only way to assure the production of happy long-lived human beings.

The sugary fruits, such as dates and bananas, and olive oil, which are digested and assimilated without effort practically, form the basis of the most perfect and healthful diet imaginable. By the use of such foods there is no undue tax upon, or wear of, the internal organs, as there is with starchy sluggish natured foods.

If the people were wise they would see that millions of extra acres of land were at once laid down to dates, bananas, and olives particularly. The oil from olives furnishes us with the finest and truest form of fat procurable. In winter even, with ample dried sugary fruits and olive oil, the bodily heat can be maintained to perfection with ease. If to the above perfectly ripe-mellowed eating apples are added, we have an unfired food combination which all the science combined will never be able to equal much less surpass.

I would here bring out a point which calls for attention. As most of the dessert apples sold by fruiterers are not half ripened, few of the public really know what a perfectly mellowed apple is. All such hardy fruits especially should be perfectly matured before they are eaten; in this condition they are easy of digestion and most nutritious. The time has come when retail fruit distributors should have a heated ripening arrangement in every store. It was through the heating rooms in the underground cellars of the Covent Garden Market wholesale banana merchants years back, for colouring up and maturing the green fingers on the bunches, that such wonderful popularity was assured for bananas.

The bland dietary I have mentioned will keep ordinary people fit, improve the health of every sufferer, and if persisted in will cure the most obstinate ailments, except where sugar should be avoided; in which case a totally different form of non-animal dietary is essential. With the provision of congenial conditions, the combination fruit-meal commended above will reduce the number of the "pus-cells" and tone up and maintain the red corpuscles at the normal standard, so that humanity may be made immune to disease in a perfectly clean and natural manner.

Huxley, Haeckel, and Metchnikoff thought they saw red through the white corpuscle; but I doubt it. Pasteur said that germs cause disease, which they do not. Sir Almroth Wright catches and cooks them, and then injects the matter (a filth food) into the system, for the purpose of feeding the "pus-cells" (filth feeders) and stimulating them to greater activity in the cure of disease.

The opinion of Paracelsus, that "A physician without the knowledge of the stars can neither understand the cause or cure of disease," is pure wisdom compared to the teachings of those who would assure the provision of clean and natural conditions by unclean and unnatural methods.

Man a Creature of Conditions.

There was a time undoubtedly when there were no filth feeding corpuscles in the blood and no filth feeding organisms in the soil. My long-continued studies in the dust have convinced me that diseases in soils, plants, and men arise from conditions brought about by the introduction of poisons and by imperfect environment; and experiments have satisfied me beyond doubt that this is the natural and correct explanation. Bacteria do not originate diseases. Their advent is always preceded by the existence of unclean conditions.

The eventual existence of filth in the animal and vegetable kingdoms brought the bacteria and micro-organisms of disease, as we know them, upon the scene. They were worse when man reached a more advanced stage. It was the more unnatural life which man in his upward progress led which paved the way for the advent of diseases in more destructive and deadly form in the animal and vegetable kingdoms. Before man and plants discarded the simple life there was no scope for the presence or activities of the "pus-cells" and of the bad bacteria, because there were no congenial conditions to entice them, and no weak corrupted internal tissue for them to feed upon. The nature, number, and activity of the "pus-cells" and micro-organisms are regulated by the kind and extent of the dietary and the environment which they enjoy.

Man is a creature of conditions. The cells, the foundation of his living structure, are creatures of conditions also. Health is a sign of conditions congenial to man. Disease is a sign of conditions congenial to micro-organisms—everywhere. Conditions regulate the advent and perpetuation of health or disease in the mineral, vegetable, and animal kingdoms. Therefore there is only one means of cure for disease, and that is the provision of congenial conditions and the consumption of pure non-inflammatory, non-fermented drinks and foods.

With flesh eating came disorganised tissue and the presence of purulent matter in the human organism. Nevertheless, things were not so bad as later, when man began to live the unnatural city dwelling life, ever since which the "pus cells" have practically become part and parcel of his nature.

When man began to eat flesh (a filth food) he began to be diseased. When he began to feed animals on manure fed grass (a filth food) he introduced "pus cells" and micro-organisms of disease into the lower animal kingdom. When he began to grow fruits, vegetables, and grains by the aid of waste animal matter (a filth food) he infected them with similar destructive agents. As the result of these threefold violations of moral law alone Nature has plagued his structure with purulent diseases, which have in the majority of cases made life a veritable curse.

In consequence of my clean culture teaching, English medical investigators of note took up the study on the Continent, having found, as others had long previously, that the wounds of soldiers who have been used to a meat dietary do not heal anything like so cleanly or quickly as do the wounds of soldiers who have been used to a fruit and vegetable dietary. They also found that the most difficult wounds to heal were those of soldiers who had been used to live upon sewage and manure grown products. I could personally quote scores of cases to prove this which have come under my personal notice. Awful dangers attend the repulsive use of dead and waste animal matters in the growth of foodstuffs. These highly fed and poisoned soils are a menace to the health of the people wherever they exist.

If clean plant foods through a clean soil produce healthy tissues in roots, fruits, and grains, and through the consumption of the latter, healthy tissue in the human body, it naturally follows that the use of unclean plant foods through an unclean soil must produce unhealthy tissue in roots, fruits, and grains, and through the consumption of the latter unhealthy tissue in the human body.

"Clean culture," writes an M.P., a member of an important Parliamentary Agricultural Committee now sitting, "is the application of the pure food principle to plant as well as to animal life." But it is more. It is the application of the pure food principle to soils also.

An authority on physical reform writes:—"It goes right to the root of the building of a healthy body. By studying what shall go to build up the foods that shall eventually build our bodies, and by insisting on the necessity of the purity of the food of the food, you have got down to the actual foundation of the food question."

Though the farmer may turn his sheep into the meadows marred by tall over luxuriant tufts of coarse grass, the sheep avoid and will not eat them, even after the pasture around them has been grazed quite bare. They know instinctively that the short succulent sugary healthy grasses are the most savoury and richer in nutrients than the tall coarse bladed stuff, which springs up where the foul carbonate of ammonia laden manure has been dumped upon the sward.

A gentleman in the West of England has written to me in high praise of the new soil science. He says, "I wish I had known of clean culture when I was in the colonies, where I passed the greater part of my life as a planter. I would have had the 'bush' burned *in situ*, and the ashes conveyed to my sugar fields. When in Barbadoes I was told that the father of Sir Graham Briggs amassed a large fortune in sugar by cutting and burying the 'bush' in his sugar fields. All his neighbours, of course, set him down as a crank. Practically he was carrying out part of clean culture teaching. In Cornwall there are potteries where the fuel for the kilns consists entirely of gorse or furze, and the ashes which result from this burning are sold at sixpence a bushel. They tell me the effect of the ashes on roses is wonderful." As a matter of fact, I might here mention that the use of these ashes for roses especially was brought about by my advice, and this advice is emphasised in my *Fortnightly Review* paper for June, 1910.

Resistless Influence of Food.

Prof. Henslow said truly that if Darwin had studied plants in a state of nature to the same extent as cultivated ones he would not have been compelled to call in the imaginary aid of Natural Selection, to correspond with the artificial aid of man under cultivation. In respect to this, the late Prof. Romanes wrote Henslow:—"If you could prove that indefinite variations have not occurred in wild plants, but only under cultivation, you would destroy Darwinianism *in toto*."

I am satisfied that there never have been indefinite variations in plants, except by and through the influence of food, but in any event Natural Selection is a chimera.

The cells of plants are endowed with different degrees of transformative energy, and they depend upon the metamorphosis of nutrient matter for their growth. The health, vigour, and characters of plants therefore are regulated by their assimilative functions. Hence food is the dominating factor in the Origin of Species.

Henslow utilises several of the opinions of Bacon and developes them, but I think in respect to the effect of moisture, drought, and high altitudes upon plant life that he errs in attributing the changes mainly to their varying influences. The dominating factor in these transformations is food.

Dr. Weismann reminds us that some arctic plants have not evidently varied since the glacial epoch. I suggest that this is because the power to vary is not stimulated until the plants enjoy a change of nutrient. True cultivation and new surroundings produce distinct transformations in the characters of wild plants; nevertheless, they are due to new supplies of food, cultivation, and new surroundings being synonymous with such.

About sixty years ago much disputation arose over a French pear. Some pomologists held that it was a distinct variety. Others that it was really the Winter Coretien. In one French district it was called by one name. In another district by a different name. In one district it was seedy, and in the other seedless always. Bacon's theory is amply vindicated in this connection. "If," he said, "you will have one plant change into another you must have the nourishment overrule the seed."

The transformation of the seedy pear of Auch into the seedless pear of the more favourable district of the south-west was due to the richer soil alone. Plethoric conditions, as I insist, affect seediness, that is fruitfulness, in the most pronounced manner.

Many years ago I exhibited quantities of beautiful sky-blue French beans to admiring crowds at Earl's Court Horticultural Exhibition. The sky-blue pods put on their new and remarkable colour only when grown in the same soil at Twickenham; consequently, it was due to food and food alone.

We are told that the life of a plant, like that of an animal, is a series of constant adjustments between internal structure and external surroundings. But in this field of investigation, again, the influence of food, the vital factor, has been ignored.

We know that leaf buds can be transformed into flower buds, that the fruit tree can be made to produce fruit or wood at will, and that floriferousness may be assumed at the expense of foliage by the marvellous influence of food.

In the stationary character of some of the arctic plants we have ample proof of the soundness of my theory, that the power to vary is not stimulated until plants enjoy a change of nutrient; then, under the influence of the responsive power of protoplasm, the transformation begins, not "accidentally" as Huxley persumed, but in strict accordance with a clear principle of biological law. It is evident, then, that variations do not occur under the continued influence of original conditions, but through a changed dietary when plants put on new characters under the awakening of the responsive power inherent in them. I close my present series with the repetition of the fact that the cry of every living thing, seen and unseen in every sphere of activity, is, "We are what our food makes us," and the recognition of that truth is essential if we would understand the nature of health, disease, cells, and living organisms.

In the first article of this series (p. 178) "James" instead of John Beattie Crozier, was written in error.

NOTE ON PURE SODIUM CHLORIDE.

By VERNON C. SHIPPEE.

Lohman in the Chemical News, cxiv., 53, described the preparation of common salt by different methods in which he found a considerable quantity of the potassium salt. Lahman made only one crystallisation from pure distilled water.

We prepared common salt by the same methods employed by Lohman, but crystallised each sample four times from distilled water, and thereby succeeded in removing most of the potassium salt.

We added pure metallic sodium to distilled water, and neutralised the caustic soda thus formed with pure hydrochloric acid, and the salt was precipitated by adding hydrogen chloride to the solution. The flame test showed a considerable quantity of potassium salt. After the four crystallisations we precipitated the potassium chloride with a solution of platinic chloride, and found less than 0·01 of a per cent of potassium chloride. The potassium must have been mixed with the metallic sodium.

We neutralised a solution of caustic soda sticks which had been purified by alcohol with pure hydrochloric acid. After the crystallisations we found 0·03 per cent of potassium chloride.

Lastly, we crystallised a portion of "C.P." common salt from the laboratory shelves. After the crystallisations we found 0·07 per cent of potassium chloride.

It was concluded that although the potassium chloride obstinately persists with the sodium chloride it can be removed by repeated crystallisations, and pure sodium chloride may be obtained for standardisation and other purposes.

Cornell College, Sept. 24, 1917.

PHOSPHOR-TIN AND A VOLUMETRIC METHOD FOR ITS ANALYSIS.

By RICHARD EDWIN LEE, W. H. FEGELY, and FRANK H. REICHEL.

The paper presented here traces its origin to a request forwarded to the Carnegie Hall of Chemistry, Allegheny College, Meadville, Pennsylvania, for a method for the rapid and accurate analysis of an alloy of phosphorus and tin, known commercially as "phosphor-tin." This material is purchased according to specifications. Analysis of each shipment therefore is desirable. Furthermore, since the correct proportions of the material to be used in the various processes can be determined only from a knowledge of its composition such an analysis is practically necessary. It is obvious, therefore, that a method corresponding to the description in the request should be available. No such method, however, was found in the literature.

In this connection it may be contended that inasmuch as the tin in the alloy can be readily determined by some standard method, such as the sulphide method, and the percentage of phosphorus estimated by the "method of difference," that the problem presented was not one difficult of solution. It should be noted, however, that the presence of any impurities in the alloy would cause a corresponding error in the calculation of the phosphorus content. This, of course, would render the procedure valueless. Obviously the problem requires for its solution the formulation of methods for the determination of both phosphorus and tin.

Properties and Use of Phosphor-tin.

The phosphorus in phosphor-tin alloys varies, as a rule, from 0·1 to 5 or 6 per cent. According to Desch ("Metallography," 1910), phosphor-tin is grouped with the so-called "brittle alloys," which are described by him as "alloys produced commercially for the purpose of facilitating the addition of small amounts of elements to molten metals. Thus, silicon and phosphorus as such are now seldom added to metals, rich alloys of these substances with iron, copper, or tin being usually employed. These rich alloys are composed principally of intermetallic compounds, as silicides and phosphides."

Phosphor-tin is manufactured on the large scale by melting tin and phosphorus in large furnaces which are frequently provided with apparatus for the partial exclusion of air. The alloy has a crystalline structure, and is very hard and brittle. In colour it resembles tin.

This alloy is used instead of tin in the manufacture of various tin alloys for the purpose of either preventing the formation of oxide or enhancing certain mechanical qualities of the alloy into which it enters. For example, in the manufacture of certain bronzes, if phosphorus is added in small amounts, it apparently does not produce, as was originally suspected, a new alloy known as phosphor-bronze. It serves simply as a deoxidising agent in the molten metal, the resulting phosphoric oxide passing into the slag or scum on the surface (Rosenhain, "Introduction to Physical Metallurgy," 1914, p. 152). When the metals entering into the composition of the alloy are melted in the absence of phosphorus the alloy is more or less seriously contaminated with oxides. It is obvious, therefore, that if the quantity of added phosphorus be carefully adjusted the resulting product is merely a purified alloy. However, if a larger quantity of phosphorus is introduced than is required when it is to function simply as a reducing agent the product is an alloy with properties distinctly different from those of the merely purified alloy.

In the manufacture of bronze, according to Desch, "if the quantity of phosphorus introduced through the medium of phosphor-tin exceeds that required for complete deoxidation by more than about 0·1 per cent it will cause brittleness owing to the separation of hard particles of the phosphide, Cu_2P. Such a mixture is sometimes very incorrectly called phosphor-bronze. If the alloys are to be employed in the manufacture of gear wheels, bearings, &c., the quantities of tin and phosphorus present vary from 6 to 15 per cent and 0·7 to 1·5 per cent respectively. These alloys are very hard and better able to resist friction. The hardness is due in part to the presence of the hard particles of copper phosphide. The presence of these hard masses in the comparatively soft matrix of lead produces the combination of great hardness with a limited but distinct plasticity which is required for such purposes."

It is not desirable, however, to enter into a detailed account in this paper of investigations in this field of ternary alloys; nor is this necessary to make it perfectly obvious that methods for the rapid and accurate chemical analysis of alloys similar to phosphor-tin are of immediate need in control work.

Preliminary Experiments showing the Behaviour of the Alloy in certain Solvents.

At the very beginning of this investigation it was concluded that it would be necessary at some stage of the work to determine whether the phosphorus in the alloy is wholly in the chemically combined or uncombined form, although it seemed rather improbable that it should exist in the latter form. Subsequent work indicated that the metalloid is present in the alloy in the form of a definite compound.

The early part of the experimental work was devoted therefore to a study of the effect of various solvents on suitably prepared samples of the alloy with the following results:—

Sulphuric acid (5N) failed to dissolve the sample, but sulphuric acid (sp. gr. 1·84) effected its immediate solution. *Hydrochloric acid* (sp. gr. 1·20) readily dissolved the alloy, but 5N acid apparently had little effect on it. *Nitric acid* (sp. gr. 1·42) decomposed the sample, leaving a white residue. When aqua regia was added to the alloy the authors were very much perplexed to find at first that the sample apparently ignited, and burned with a blue flame. It may be noted here that it was this rather unexpected behaviour which later suggested the proposed method for the solution of our problem.

Having ascertained how to effect the solution of the alloy it was decided to attempt quantitative determinations of tin and phosphorus, using sulphuric acid (sp. gr. 1·84) as a solvent, with a view to determining whether all of the phosphorus was liberated as phosphine, or whether it was partially oxidised to phosphoric acid.

One-half grm. of the sample was dissolved in 10 cc. of sulphuric acid (sp. gr. 1·84), and evaporated to 7 cc. The solution was then diluted with 150 cc. of water, and saturated with hydrogen sulphide. The precipitate of tin sulphide was filtered on a weighed Gooch crucible, dried, and finally ignited to the oxide, and weighed. The phosphoric acid in the filtrate was then determined. As the sulphuric acid would eventually act as an interfering substance it was precipitated as barium sulphate, using barium nitrate as the precipitant. The barium sulphate was filtered off, washed, and rejected. To the filtrate, heated to 85°, 50 cc. of ammonium molybdate solution were added. The precipitate of ammonium phosphomolybdate was filtered on a weighed Gooch crucible, dried at 110°, and weighed. From the weight of this precipitate the percentage of phosphorus was calculated. The determinations of the tin by the method outlined checked within satisfactory limits, but the results obtained from the phosphorus determinations were not concordant, the conclusion being that varying portions of the phosphorus were oxidised during the process of solution. Concentrated sulphuric acid was therefore abandoned as a solvent for the alloy.

Solution of the sample in hydrochloric acid proved to be the real starting point of the method presented in this paper. A 0·5 grm. sample of the alloy was treated with hydrochloric acid (sp. gr. 1·20). It dissolved rapidly with the evolution of phosphine. The solution was evaporated to 10 cc., diluted with 100 cc. of water, and saturated with hydrogen sulphide. The precipitate of tin sulphide was filtered out on a weighed Gooch crucible, washed, ignited, weighed as the oxide, and the tin calculated as before. The series of results obtained checked very closely with those obtained when sulphuric acid was used as a solvent. This standard procedure for determining tin was used in the early stages of the work to check the determinations of tin by the proposed method. Further confirmation of these results were secured later by the electrolytic method.

The filtrate from the tin sulphide was heated to remove hydrogen sulphide, then neutralised with ammonium hydroxide, and magnesia mixture added. Six separate tests failed to show evidence of the presence of phosphoric acid, even after twenty-four hours.

With the evidence at hand indicating that the phosphorus is evolved quantitatively in the form of phosphine when the alloy is dissolved in hydrochloric acid, the solution of one phase of the problem, namely, the determination of the phosphorus content, was anticipated if a method could be formulated by which the gas might be absorbed and oxidised to phosphoric acid.

Development of Method for Determining Phosphorus.

A variety of solutions have been employed in gasometric methods for absorbing phosphine quantitatively. Only two of those suggested, however, were found suitable, owing to the nature of the procedure involved. These two were bromine water and a solution of potassium permanganate.

The *apparatus* used consisted of a Florence flask of 500 cc. capacity fitted with a 3-holed rubber stopper through which a 100 cc. tap-funnel and two pieces of glass tubing bent at right angles were inserted. For the absorption train three Erlenmeyer flasks of 150 cc. capacity were connected in series with the Florence flask.

Aqueous Solutions of Bromine.—To each of the Erlenmeyer flasks 100 cc. of bromine water were added. The train was connected to the evolution flask in which a 0·5 grm. sample of the alloy was placed. Hydrochloric acid (sp. gr. 1·20) was added to decompose the alloy. The greater part of the bromine in the first absorption flask disappeared before that in the second flask was attacked, owing to the rapid absorption and oxidisation of the phosphine. The evolution flask was finally freed from phosphine by sweeping out the system with natural gas or carbon dioxide. By this latter procedure most of the remaining bromine was displaced from the water solution and escaped into the laboratory. Owing to the well known irritating action of bromine vapours on the respiratory passages it was thought that the use of bromine water as an absorbent might not be regarded as entirely satisfactory for routine analytical work. Nevertheless, four analyses were made. The phosphoric acid in each flask was determined separately to be sure that no phosphine escaped the last flask in the train, it having been shown that none remained in the hydrochloric acid solution in the evolution flask.

The contents of the three flasks in which the respective delivery tubes had been rinsed were transferred to beakers marked Nos. 1, 2, and 3, corresponding to the positions in which the flasks were located in the train. The phosphoric acid present in each flask was determined by a standard procedure with the results given in Table I.

TABLE I.—*Retention of Phosphine by Aqueous Solutions of Bromine.*

	Per cent phosphorus found in Flasks No.—			
	1.	2.	3.	Total.
Experiment 1 ..	2·69	0·32	0·00	3·01
Experiment 2 ..	2·91	0·07	0·00	2·98
Experiment 3 ..	2·87	0·16	0·00	3·03
Experiment 4 ..	2·51	0·50	0·00	3·01

The absence of phosphorus in the third absorbing flask indicates that no phosphine escaped.

Although it appears that bromine water may be used for routine work with satisfactory results if operations are conducted in a hood, or if a trap is provided to prevent the escape of bromine vapour, it was abandoned as an absorbent for one which proved more suitable. This was a solution of potassium permanganate.

Aqueous Solution of Potassium Permanganate.—The use of a solution of potassium permanganate as an absorbent of phosphine with its ultimate oxidation to phosphoric acid, H_3PO_4, immediately suggested the attractive procedure of determining the phosphorus by titration of the excess of a known quantity of a standard solution of the substance. Unforeseen difficulties were encountered, however, when an effort was made to conduct the analysis according to the foregoing scheme.

The hydrochloric acid which is used as the solvent for the alloy tended to pass over into the absorbing flasks where it decomposed the permanganate. This fact made it necessary to search for another absorbent which would trap the hydrochloric acid, but not the phosphine. Water and aqueous solutions of sodium hydroxide, sodium carbonate, and ammonium hydroxide were tested separately with respect to the property of absorbing the two gases. All of these substances were found to absorb hydrochloric acid gas as fast as it was evolved; but unfortunately they absorbed phosphine also. This was shown by adding bromine to the solutions to oxidise the phosphine to phosphoric acid, and then precipitating the latter. Sodium hydroxide dissolved the most phosphine, and water the least. In all cases, however, enough was dissolved to make the results valueless. Other solutions were tested in similar respects, but the results obtained were no more encouraging. Finally, the search for an absorbent which would prevent the passage of the hydrochloric acid into the permanganate solution and at the same time be inert as regards its action towards phosphine was abandoned. This meant, of course, the relinquishing of the scheme whereby the excess or unused portion of permanganate was to be titrated and the substituting of a procedure providing for the precipitation of the phosphoric acid from the absorbing solution of potassium permanganate.

With the adoption of the method of the ultimate precipitation of the phosphorus as phosphoric acid the next problem that presented itself was the determination of that concentration of the absorbing solution which would prove most efficient. It was thought advisable, however, to employ a solution of such concentration that all of the phosphine would be absorbed in the solutions in the first two of the three absorbing flasks as this would provide for a relatively large margin of safety when analysing new alloys.

The best concentration of permanganate to be used in the analysis of alloys containing a given percentage of phosphorus was determined by a series of experiments in which a moderately concentrated solution was used at first, followed by the gradual reduction of the concentration of the solution in each succeeding experiment until phosphoric acid was found in the absorbent in the third flask. In each of the determinations in the series reported in Table II., using sample No. 1 of the alloy, 90 cc. of potassium permanganate solution of known concentration were introduced into each of the three Erlenmeyer absorption flasks, after which the experiment was conducted in the same manner as when an aqueous solution of bromine wa employed as the absorbing agent.

TABLE II.—*Retention of Phosphine by an Aqueous Solution of* $KMnO_4$.

No.	Grms. $KMnO_4$ in 270 cc. of absorbing solution.	Per cent phosphorus found. Flask No. 1.	2.	3.	Total.
1.	3·0000	3·01	0·02	—	3·03
2.	2·5000	2·90	0·09	—	2·99
3.	2·0000	2·76	0·25	—	3·01
4.	1·5000	2·73	0·28	—	3·01
5.	1·0000	2·74	0·29	—	3·03
6.	0·5000	2·61	0·39	—	3·00
7.	0·2500	1·87	1·01	0·16	3·04

From the data in Table II. it was concluded that a concentration of 0·5 grm. of potassium permanganate in 270 cc. was necessary for the complete absorption of the phosphine in the first two flasks. But since the percentage of phosphorus in different samples varies ordinarily from 2 to 6 per cent it was thought advisable to employ a solution containing 1 grm. in 270 cc.

Effect of the presence of Nitric Acid in the Permanganate Solution.—Following the absorption of the phosphine by the potassium permanganate solution and its ultimate oxidation to phosphoric acid, about 30 cc. of nitric acid (sp. gr. 1·42) were added to the 270 cc. of solution preparatory to the precipitation of the phosphoric acid. It occurred to the authors that if the nitric acid were added to the absorbing solution before the phosphine was introduced, it might be possible to use an absorbing solution with a smaller concentration of potassium permanganate. The series of experiments reported in Table III. show how well the suspicion was founded.

TABLE III.—*Retention of Phosphine by a Solution of* $KMnO_4$ *and* HNO_3.

No.	Grms. $KMnO_4$ in 270 cc. of absorbing solution containing 30 cc. HNO_3.	Percentages phosphorus found. Flask No. 1.	2.	3.	Total.
1.	0·5000	3·00	0·03	—	3·03
2.	0·4500	2·96	0·03	—	2·99
3.	0·4000	2·97	0·04	—	3·01
4.	0·3500	2·89	0·11	—	3·00
5.	0·3000	2·92	0·10	—	3·02
6.	0·2500	2·64	0·35	—	2·99
7.	0·2000	2·02	0·87	0·12	3·01

The increase in the absorbing and oxidising power of this solution over the potassium permanganate solution is probably not due merely to the oxidising action of the nitric acid but to reactions into which it enters or effects. For example, nascent chlorine is introduced into the system by the action of the nitric acid on the hydrochloric acid which distils over from the acid in the evolution flask. Other reactions probably occur also. At least three strong oxidising agents, potassium permanganate, nitric acid, and nascent chlorine are acting together under the conditions of the procedure.

Procedure Used in Checking Proposed Method for Determining Phosphorus.

The authors have attempted so far to show experimentally that the phosphorus present in phosphor-tin is probably in the form of a phosphide, that on solution of the alloy in hydrochloric acid it is liberated quantitatively as phosphine, and that this latter substance may be entirely absorbed and oxidised in certain solutions, and later determined as phosphoric acid. At this stage of the work, with a view to determining the accuracy of the proposed method for determining phosphorus, a portion of Sample 1 was analysed by the long and rather tedious but well known procedure, commonly known as the cyanide method. This method is sometimes employed in the determination of phosphorus in the phosphor bronzes when accuracy is the chief consideration. The liberation of hydrocyanic gas at one stage of the method also contributes to its lack of popularity. The results obtained by use of the cyanide method were slightly but uniformly lower than those obtained by the rapid method proposed in this paper. This has been attributed to the large number of filtrations required by the older method.

Cyanide Method.—The procedure used by the authors in making the analyses of the alloy by the cyanide method was as follows:—To 0·5 grm. alloy in a 200 cc. beaker, 25 cc. nitric acid of sp. gr. 1·42 were added. The beaker was covered with a watch-glass, and after the first violent action had ceased it was placed on a water-bath, and heated until the alloy was completely decomposed, and the residue was entirely white. All the phosphoric acid remains with the tin as stannic phosphate.

The nitric acid solution of the alloy was diluted, and the stannic oxide containing the phosphoric acid was filtered off, washed several times, and dried. The precipitate was transferred to a crucible, and mixed with three times its weight of potassium cyanide. The crucible was covered and the mass fused a few minutes at red heat. On cooling, the fused mass was extracted with hot water, filtered, and the paper washed with hot water.

The hydrocyanic and cyanic acids were expelled from the filtrate by boiling with concentrated hydrochloric acid. The solution was evaporated to dryness to dehydrate the silicic acid which had been dissolved from the porcelain crucible. The dry residue was dissolved in a little hydrochloric acid, and hydrogen sulphide passed through the solution to precipitate small amounts of tin likely to be present. The precipitate was filtered off and washed, and the hydrogen sulphide destroyed in the filtrate by adding bromine water, and boiling. The phosphoric acid was then precipitated, ignited, and weighed as the pyrophosphate.

Twelve phosphorus determinations were made by this method. The results of these determinations are given in Table V.

Development of the Method for Determining Tin.

A survey of the methods proposed for the determination of tin in alloys will reveal the fact that the majority of those possessing accuracy require considerable time for their execution. Even the sulphide method is regarded as being comparatively long and tedious when considered from the standpoint of the analyst doing routine work. It was recognised therefore at the very beginning of the work that the attractiveness of any proposed method would be greatly enhanced if it provided for a rapid and accurate determination of tin in the alloy.

In considering the problem at this stage of the work the authors were led naturally to an investigation of the solution of the alloy from which the phosphorus had been liberated as phosphine with a view to ascertaining if it could be used in determining the tin either gravimetrically or volumetrically.

It is well known that tin dissolves in hydrochloric acid in the absence of oxidising agents with the formation of stannous chloride. It was this reaction which suggested the point of attack, namely, the problem of dissolving the sample of alloy used in the phosphorus determination in such a manner that the tin should be left in the hydrochloric acid solution (in the generating flask) in the "ous" condition. If this could be accomplished the solution of the problem was indicated, for all that would then be required to complete the determination would be the titration of this stannous chloride solution with a suitable standard oxidising solution.

As the result of the experimental work following the lines of inquiry suggested in the previous paragraph, it was found that if the system of apparatus used in the phosphorus determination was swept free from air before and after the liberation of phosphine by the use of illuminating gas, carbon dioxide, or any other gas inert as regards the stannous chloride, (1) the phosphor-tin dissolved in hydrochloric acid with the quantitative formation of phosphine and stannous chloride, and (2) it was possible to determine the amount of tin present by adding to the solution a slight excess of pure ferric chloride and determining the amount of reduction by titrating with a solution of potassium dichromate.

Using this procedure a number of series of determinations of tin in Sample 1 were made. The results were in close agreement with those obtained in the preliminary experiments when the sulphide method was used to determine the tin content of the different samples of the alloy. The results given in Table IV. indicate the relative accuracy of the method.

Table IV.—*Determination of Tin in Phosphor-tin*

	Sulphide method.	Proposed method.
Experiment No. 1 ..	96·30	96·35
Experiment No. 2 ..	96·38	96·42
Experiment No. 3 ..	96·34	96·37
Experiment No. 4 ..	96·39	96·41
Experiment No. 5 ..	96·37	96·43
Average	96·36	96·40

Although the foregoing data indicated that the proposed method possessed an accuracy comparable to that of the sulphide method it was deemed advisable to secure further confirmation of the probable tin content of the alloy. With this in view an electrolytic method was used in the final series of test experiments to check results obtained by the method proposed in this paper for the determination of tin.

Procedure used in Checking Proposed Method for Determining Tin.

According to Smith ("Electro-analysis," 1911, 171), tin may be deposited electrolytically from a stannous or stannic ammonium chloride solution containing an excess of a hot saturated solution of ammonium oxalate. Therefore, instead of titrating the hydrochloric acid solution of stannous chloride in the evolution flask it was cooled at this point, and then neutralised with ammonium hydroxide. The precipitate which formed was dissolved with hydrochloric acid, and 100 cc. of a hot saturated solution of ammonium oxalate were added. This solution was then electrolysed, using a rotating anode and a tared platinum dish (previously coated with silver or copper) as the cathode. A current of $N.D._{100} = 5$ ampères and 9 volts was applied for one and one-half hours.

The results obtained by the procedure just described confirmed those given by both the sulphide method and the proposed method. These results are tabulated in Table V.

Solutions used for Determining Tin Standard Potassium Dichromate Solution.—4·1248 grms. of C.P. crystals dried at 105° were dissolved in water, and the solution made up to 1 litre. The solution was standardised by means of pure ferrous ammonium sulphate. One cc. of this solution was found to be equivalent to 0·005 grm of tin.

Indicator.—The potassium ferricyanide solution used for determining the end-point in the titration with the dichromate solution was prepared just prior to use. A crystal of potassium ferricyanide about the size of a pea was dissolved in about 75 cc. of distilled water. When a drop of this solution was mixed with a drop of ferric chloride only a light brown colour was produced.

Solutions used for Determining Phosphorus.

Absorbing Solution of Potassium Permanganate.—Two grms. of the pure salt in 1 litre.

Ammonium Molybdate.—This solution was prepared by one of the well known standard procedures (Blair, "Chemical Analysis of Iron," 1912, 997).

Wash Solution of Acid Ammonium Sulphate.—To 1 litre of water, 16 cc. of ammonium hydroxide (sp. gr. 0·90) and 25 cc. of sulphuric acid (sp. gr. 1·84) were added.

Standard N/10 Solution of Potassium Permanganate.—3·163 grms. of C.P. potassium permanganate were dissolved in water, and the solution made up to 1 litre. It was standardised by means of pure ferrous ammonium sulphate; 1 cc. of this solution was equivalent to 0·00008829 grm. of phosphorus.

Procedure for Analysis of Alloy.

Sawings were taken from the material to be analysed. Any iron introduced by abrasion of the saw-blade was removed by drawing a magnet over the sawings spread in a thin layer. Sawings are to be preferred to drillings as the latter are quite coarse owing to the brittleness of the alloy.

A 0·5 grm. sample of the alloy was put into the Florence flask. Any fine particles of the phosphor-tin adhering to the walls of the flask were rinsed down with a jet of water. The rubber stopper, through which the two tubes bent at right angles and the tap-funnel are inserted, were fitted tightly into the mouth of the Florence flask.

To each of the three absorption flasks assembled as a train, 90 cc. of the potassium permanganate solution and 10 cc. of nitric acid (sp. gr. 1·42) were added. The train was connected with the Florence flask with a short piece of rubber tubing. Carbon dioxide or illuminating gas was then directed through the system for three minutes to sweep out the air, and the inlet then closed with a pinchcock; 30 cc. of hydrochloric acid (sp. gr. 1·20) were transferred to the tap-funnel, the stopcock was opened, and the hydrochloric acid allowed to run into the flask. The stopcock was immediately closed, and heat applied to the flask. The boiling-point should be reached in about five minutes and maintained until the alloy is completely decomposed. When the alloy was dissolved the Bunsen burner was removed and carbon dioxide or illuminating gas was again forced through the system for three minutes, so that any traces of phosphine in the Florence flask would be swept into the permanganate solution. Without stopping the flow of gas the absorption train was disconnected from the Florence flask. The tin remains as stannous chloride in the Florence flask, and the phosphorus is found as phosphoric acid in the absorption flasks.

One or 2 grms. of ferric chloride which gave no test for ferrous iron were added immediately to the contents of the generating flask, and the solution was titrated at once with potassium dichromate, using potassium ferricyanide as an external indicator. By determining the amount of ferric iron reduced by the stannous chloride the amount of tin present was easily ascertained (1 cc. of the potassium dichromate solution as prepared was equivalent to 1 per cent of tin when a ½ grm. sample was used).

The contents of the three absorption flasks were then transferred to a 500 cc. Florence flask. The permanganate solution was boiled one minute. It was then removed from the hot plate, and potassium nitrite was added in small portions until the excess permanganate was reduced and the solution was colourless. It was then boiled one minute to expel any nitrous acid that might be present since it acts as an interfering substance later on in the procedure.

The solution was removed from the hot plate, and cooled to about 50° by placing in a cooling bath, after which it was made slightly alkaline with ammonium hydroxide. When the neutral point was reached a heavy precipitate of manganese phosphate formed which served as an indicator at this point. This precipitate was just dissolved with nitric acid (sp. gr. 1·42) and 10 cc. added in excess. The solution was heated to a temperature of 85°, and 50 cc. of filtered ammonium molybdate were added. The temperature must not exceed 85°, because of the possibility of molybdic acid being precipitated. The contents of the flask were vigorously stirred for five minutes. The yellow precipitate of ammonium phosphomolybdate was filtered off and washed with acid ammonium sulphate solution until 2 or 3 cc. of the washwater did not give a brown coloration on the addition of a drop of ammonium sulphide; 7 cc. of ammonium hydroxide of sp. gr. 0·90 and 15 cc. of water were poured into the flask in which the precipitate was formed, to dissolve any adhering precipitate; the solution was then poured on the precipitate in the filter. The filtrate containing the ammonium molybdate and ammonium phosphate was next prepared for the Jones reductor. The filter was washed with water until the filtrate had a volume of about 60 cc.; 10 cc. of sulphuric acid (sp. gr. 1·84) were added. (If a precipitate forms on the addition of the sulphuric acid it should be redissolved with ammonium hydroxide and the same amount of sulphuric acid added a second time).

The solution was then passed through a Jones reductor charged with amalgamated zinc. It was passed through a second time after the addition of 2 cc. more of sulphuric acid. This was followed with 200 cc. of water. The solution collected from the reductor was titrated at once with N/10 potassium permanganate.

Test Experiments.

In order to show the relative accuracy of the proposed method, two different samples of phosphor-tin were used in making the following series of determinations of tin and phosphorus:—Twelve different portions of Sample I. were analysed for phosphorus and tin, six by the recommended procedure and six by the standard procedures described in the body of this paper. This series was then followed by a similar series of analyses in which Sample II. was used.

TABLE V.—*Results of Analyses of Phosphor-tin.*

		Percentages tin found.		Percentages phosphorus found.	
Sample No.	No.	Electrolytic method.	Proposed volumetric method.	Cyanide method.	Proposed evolution method.
I.	1.	96·32	96·38	2·97	3·03
	2.	96·34	96·40	2·98	3·02
	3.	96·38	96·35	2·98	2·99
	4.	96·38	96·36	2·96	3·04
	5.	96·36	96·40	2·99	3·01
	6.	96·40	96·35	2·95	3·02
II.	1.	96·50	96·45	3·10	3·12
	2.	96·46	96·52	3·07	3·11
	3.	96·52	96·50	3·09	3·11
	4.	96·44	96·48	3·06	3·10
	5.	96·50	96·45	3·08	3·13
	6.	96·48	96·50	3·07	3·12

Summary.

The need of a method formulated specifically for the analysis of the alloy (phosphor-tin) has been shown, and attention has been called to the fact that the related literature apparently does not contain such a method.

A volumetric method has been developed and is proposed in the foregoing discussion. The tests to which this method has been subjected indicate that it is not only easy of execution but that it is also rapid and accurate.

The method provides for the carrying out of the determinations in a train of flasks. The alloy is dissolved in hydrochloric acid in the first flask, from which all air is excluded by means of a current of illuminating gas or carbon dioxide. The tin dissolves as stannous chloride and the phosphorus is liberated as phosphine, which is absorbed by solutions in the train of three flasks. The tin is titrated at once with an oxidising solution. The phosphine is converted into phosphoric acid by the absorbing solutions, from which the acid is precipitated as phosphomolybdate, which is then reduced in a reductor and finally titrated.

The time required for making the two determinations, after the sample is weighed, need not exceed forty-five minutes. Other methods, adapted to phosphor-tin analysis and giving the same order of accuracy, required hours for their execution.

The proposed method provides for the detection of impurities in the alloy. It is therefore as well adapted for careful assay work as for "control" analyses.

As a result of the study of various absorbing agents, it has been shown that potassium permanganate solutions are satisfactory absorbents for phosphine. And, furthermore, it appears that the oxidising and absorbing power of the reagent is increased in a marked degree by the addition of nitric acid.—*Journal of Industrial and Engineering Chemistry*, ix., No. 7.

A STUDY OF THE SYRUP PRECIPITATE IN WHITE SUGAR MANUFACTURE.

By CHARLES E. COATES and L. C. SLATER.

ALTHOUGH the manufacture of white sugar direct from the cane has been carried on to some extent in Louisiana for nearly a century, for certain reasons this industry has lately taken on a new lease of life, and at the present time is of great importance. To such a degree is this true, that most of the larger Louisiana sugar houses are now equipped for the direct manufacture of white sugar without the intervention of the bone-black refinery, and in many instances have installed apparatus which has proven valuable in the manufacture of beet sugar.

The experience of the last few years, however, would indicate that there are not only different chemical difficulties to overcome, but also certain mechanical differences in the manufacture of white granulated beet sugar and cane sugar, which make special detailed attention to the latter exceedingly necessary. For instance, leaving aside the important question of clarification, it has become evident that filtration of the clarified cane juice is imperative, but the method of filtration and the number of filtrations are points still somewhat in dispute.

Some sugar houses allow the clarified juice to settle and pass the decanted, clear juice through bag filters. Occasionally the filtered juice is filtered again before final evaporation, but ordinarily it passes direct to the effects, where it is evaporated to a Brix of from 50 to 55°. There is considerable difference of opinion as to the proper subsequent treatment of this syrup. Sometimes a little sulphur dioxide or phosphoric acid is added to restore the initial acidity, but usually the syrup is passed into tanks, where it is allowed to settle from two to four hours, gradually falling in temperature during that time. When the syrup is finally drawn from the tanks there is alway to be found a precipitate, which is separated as well as possible by decantation. In certain houses the attempt has been made to filter the syrup through leaf presses. This gives a bright filtrate, but the process, being tedious and expensive, is ordinarily dispensed with, though something is always removed from the syrup. If what it removes does no harm in the subsequent manufacture of white sugar from the cane it is evident that syrup filtration could be safely omitted and the cost of manufacture lessened.

The syrup precipitate is probably not present in the solid form in the freshly evaporated syrup, inasmuch as it will form in the course of several hours in syrup which has been previously filtered, hot, through paper. It is not easy to get a satisfactory sample of the precipitate, which is gummy and difficult to obtain in a state of purity, but owing to the courtesy of two factories the writers succeeded in obtaining samples for preliminary investigations.

In Factory No. 1 the process of clarification was as follows:—The juice was obtained by 9 rollers and a crusher, about 5 per cent maceration being employed. The extraction was relatively low, being 77 per cent on the weight of the cane. The purity of the juice was fairly high for Louisiana, being about 83. Sulphur dioxide was run into the raw juice until the acidity was raised to the equivalent of 4 cc. of N/10 potassium hydroxide for every 10 cc. of juice, phenolphthalein being used as an indicator. Slaked lime was next added until the acidity was reduced to 1 cc. The juice was then heated, passed through a continuous settling apparatus, and the clear juice filtered over sand. The filtrate was not particularly bright. The juice was next passed to the effects and concentrated to a Brix of about 53°. It was then run to the settling tanks, where, in the course of a few hours, a gelatinous precipitate settled. These settlings were removed, as far as possible, by decantation, and it is this precipitate which is the subject of this study.

In Factory No. 2 there were also 9 rollers and a crusher, with a saturation of about 10 per cent and extraction of about 79. The juice had a purity of about 84·5. It was sulphured to an acidity of 9 cc., which was exceedingly high (in the writers' judgment considerably too high), then limed back to an acidity of 1 cc. and passed through heaters to a continuous settling apparatus. The clear juice was passed through bag filters, and thence to the feed tanks for the effects, where phosphoric acid was added until the acidity was raised to 1·4 cc. It was then passed to the triple effects, where it was evaporated to a Brix of about 53°. The syrup was then heated to boiling with live steam, and slowly passed through a battery of inclined, continuous separators, being about four hours in transit. During this time a precipitate settled at the bottom of the separators, which precipitate is the second one included in this study.

Both of these factories made white sugar. It will be noted that in the first factory no phosphoric acid was used in the clarification. In the second factory phosphoric acid was added to the clear juice after it had passed through the bag filters. Ordinarily, when phosphoric acid or sodium phosphate is used it is added before the juice is filtered. This precipitate seems, however, to occur normally in the syrup at all sugar houses. It forms quite slowly, usually taking several hours before it can be noticed. In one instance a perfectly bright, bag-filtered syrup stood five hours in a test-tube before the precipitate became evident, though it eventually deposited a fairly large quantity. As stated, in order to get rid of this precipitate, the syrup is sometimes filtered through some form of leaf filter press, but after a time the filter cloths get hard and crack, thus necessitating a considerable expenditure for filter cloth. Moreover, the gelatinous nature of the filtrate makes filtration slow, so that many factories prefer to omit syrup filtration entirely.

The sample of the settlings obtained from Factory No. 1 was filtered through paper and washed with cold water until the filtrate was practically without optical rotation. The precipitate was then removed, shaken several times with cold water and refiltered, the filtrate finally running clear. The same process was repeated with the settlings from Factory No. 2. The results are indicated in the following tables of analysis. For the sake of clearness each set of analysis will be followed by the comments bearing on it specifically.

Table I.

	Factory No. 1.	Factory No. 2.
Total amount of wet precipitate (grms.)	71·5	—
Total smount of air dry (grms.)	—	32
Water (per cent)	45	13
Total amount of dry matter (grms.) ..	39·3	27·7

It was impossible to estimate just how much of the original syrup this precipitate represented. In No. 2, however, we received a 50 l. carboy of the settlings from which we secured 27·7 g. dry precipitate. Taking the specific gravity of the syrup at 1·25, 50 l. equals 62,500 g. The precipitate, therefore, is about 0·04 per cent of the settlings, and as these represent a much larger amount of juice, it is probable that the percentage of precipitate in the unfiltered syrup would be less than 0·01 per cent. The precipitate is so voluminous that the amount present seems much greater than it really is.

The dry precipitate was pulverised, extracted with ether and ignited, the loss in weight on ignition being taken as organic matter. The ether extract proved to be largely, if not entirely, cane wax.

Table II.

	Factory No. 1.	Factory No. 2.
Ash in percentages	58	75·6
Organic matter in dry precipitate	42	24·4
Ether extract	—	2·6

The excess of ash in No. 2 over No. 1 proved to be mainly calcium phosphate, as shown in Table III., due to the use of phosphoric acid in clarification in one case and not in the other.

Part of the precipitate was ashed, boiled with concentrated hydrochloric acid, and evaporated to dryness. The silica was filtered off and the filtrate made alkaline with ammonia. The ammonia precipitate was filtered off and weighed. In each case considerable copper was found in the filtrate.

Table III.

Percentages in ash.	Factory No. 1.	Factory No. 2.
SiO_2	75·3	53·7
Ammonia precipitate, $P_2O_5.CaO.Fe_2O_3.Al_2O_3$ . ..	5·3	34·5
CaO in filtrate	8·0	4·1
Cu..	11·3	1·2
Total P_2O_5	0·6	13·5
(SO_4)	4·0	0·0

The large excess of silica in No. 1 may have been due to the use of sand filtration. It seems to have been present as colloidal silicic acid. The large amount of copper in No. 1 was doubtless due to an imperfect sulphur stove, which delivered the gas hot and probably with an excessive amount of SO_3; the resulting sulphuric acid seems to have attacked the various copper coils in the subsequent flow of the juice and syrup. As a matter of fact the copper was found badly pitted at the end of the campaign. Just how the copper was finally precipitated is not clear, especially since 50 grms. of the mother liquor from the settlings gave no test for copper when asked. In No. 2, where the sulphur stove was working well, the amount of copper in the precipitate was small, although there was an excessive amount of sulphur dioxide added in the sulphuring. This view is borne out by the fact that there was a fair amount of SO_4 (probably as $CaSO_4$) in No. 1, which was absent in No. 2.

In discussing the sulphitation process for white sugar making, the objection has been raised in Java that the sulphurous acid corrodes the coils. This has not been the Louisiana experience. When such corrosion does appear in excess it has been ascribed by some to sulphuric, rather than to sulphurous, acid. This does not seem very probable, in our opinion. It might be noted here, however, that the coils used in sulphitation and the effect tubes as well are uniformly made of copper in Louisiana. In one instance brass tubes were substituted for copper tubes in a quadruple effect, evaporating juice of about 5 cc. initial acidity. These brass tubes corroded badily, though the writers understand brass has been successfully used in alkaline clarification in the beet sugar houses.

In Table III. the ammonia precipitate in Sample No. 1 proved, on analysis, to be mainly oxides of iron and aluminium together with what phosphoric acid was present. The excessive iron content was probably due to the poor sulphitation. In Sample No. 2 the precipitate contained little iron. Since in tricalcium phosphate the ratio of $(CaO)_3$ to the (P_2O_5) is 168 to 141, the precipitate is probably tricalcium phosphate with a little iron and aluminium phosphate, and possibly some calcium silicate. As no sulphuric acid was present, it is evident that the excess calcium in the filtrate must have been originally present as insoluble salts of some organic acids.

After filtering off the first settlings through paper the filtrate from No. 2 was corked and heated on a water bath in order to sterilise it. After an hour or so a second precipitate separated out. This was filtered off, washed until the washing showed no optical activity, dried, and analysed with the following results:—

TABLE IV.

Total amount of dry precipitate (grms.) ..	1·6
Ash (per cent)	67·8
Organic matter (per cent)	32·2
SiO_2 in ash	26·4

The filtrate from the SiO_2 gave a heavy precipitate with ammonium hydroxide which proved to be tricalcium phosphate. The filtrate from this in turn contained a quantity of calcium. The determinations of calcium and phosphoric acid were accidentally lost, but it will be noticed that in addition to the calcium phosphate there was also an excess of calcium which must have been present as calcium silicate, or as calcium salts of organic acids. Why this precipitate formed at all is not clear. The syrup stood a couple of days before it was heated and was perfectly bright. The flocking of the precipitate took place as soon as the temperature of the water bath was reached. A possible inference from this might be that when syrup is run into settling tanks and allowed to stand the precipitate will form faster and more completely if the syrup is kept hot.

In order to get some clue as to the nature of the organic matter present in the precipitate, the following tests were made, the calculations being reduced to the basis of dry matter. The polariscope readings are in degrees Ventzke for 10 grms. of dry matter in 100 cc. reading in a 20 cc. tube. Reducing sugars were determined by weighing the reduced copper.

The moist precipitate was shaken thoroughly with cold water and filtered.

TABLE V.

	Factory No. 1.	Factory No. 2.
Direct reading	—	0·4°
Invert reading	—	0·3°
Reduced sugars (per cent) ..	Trace	0·0

Some of the moist settlings were boiled six hours on the water bath with frequent shakings, cooled, and filtered from the insoluble precipitate. The filtrate gave the following figures:—

TABLE VI.

	Factory No. 1.	Factory No. 2.
Direct reading	−0·3°	−0·5°
Invert reading	−0·4°	−0·6°
Total solids in solution (per cent)	1·7	3·9
Ash in same (per cent)	0·4	2·0
Reduced sugars (per cent) ..	Absent	0·03
Reduced sugars when hydrolysed as from dextrin (per cent) ..	—	0·11

From the composition of the aqueous extracts in Table V. and VI. it may be inferred that the organic matter of the settlings contained little or no soluble sugar, gums, or dextrins, but that a fairly constant quantity of a levo-rotatory substance was present, which was not a sugar. The residues from the water extracts were washed into a beaker with dilute hydrochloric acid, heated on the water bath for three hours, and filtered from the insoluble residue. This filtrate was made neutral with sodium hydroxide and filtered from the resulting precipitate. The results were as follows:—

TABLE VII.—*Hydrochloric Acid Digestion.*

	Factory No. 1.	Factory No. 2
Polariscope reading	0·0°	0·0°
Reducing sugars (per cent) ..	0·182	0·256

The digestion effected only a light hydrolysis as indicated by the slight increase of reducing sugars, which may have come from fragments of fibre.

TABLE VIII.—*Sodium Hydroxide Precipitate.*

Percentages.	Factory No. 1.	Factory No. 2.
Ammonia precipitate	—	19·0
CaO in filtrate	—	2·4
Total CaO, in ammonia precipitate ..	—	6·1
Total P_2O_5, in ammonia precipitate ..	—	4·0

This precipitate was redissolved in hydrochloric acid and aliquot portions analysed.

The ratio of the P_2O_5 and the total CaO to the total ammonia precipitate makes it probable that more than half the calcium was present as a salt of some organic acid.

The residue insoluble in dilute hydrochloric acid was washed, dried at 110° C., extracted in ether, and ashed.

TABLE IX.

Percentages.	Factory No. 1.	Factory No. 2.
Organic matter	Present	16·8
Ash	Present	83·2
Ether extract	Present	5·1
SiO_2 in ash	96·5	98·1

The ether extract was recrystallised from hot alcohol. It proved to be a saturated alcohol of high molecular weight, m.p. 81° C. It was clearly cane wax, probably present in a fine emulsion and carried down by the coagulated silicic acid. In ashing the residue there was an odour somewhat like that of burning feathers, but there was not enough material at hand to carry the investigation further.

As mentioned before, the filtrate from No. 2 settlings gave a second precipitate on being heated (see Table IV.). Part of this precipitate was heated on the water bath for several hours with dilute hydrochloric acid and filtered from the insoluble residue, which was almost entirely silica. The filtrate was made alkaline with sodium hydroxide, which gave a precipitate as before. This was filtered off, redissolved in hydrochloric acid and analysed. The filtrate from the sodium hydroxide precipitate showed neither optical activity nor the presence of reducing sugars, but showed 4·2 per cent CaO. The precipitate proved to be nearly pure tricalcium phosphate. A rough proximate analysis of Precipitate 2A would be as follows:

TABLE X.

SiO_2 (per cent)	25
Tricalcium phosphate (per cent)	40
Calcium salts of organic acids (per cent) ..	35
Gums and sugars	Absent

In every instance the filtrate from the sodium hydroxide precipitate in 2A was coloured, the alkaline solution being strongly purple; in neutral solution it was bright green, in acid light reddish yellow. The colour change was exceedingly sharp. It was thought at first that this colouring had been developed by hydrolysis, possibly of some member of the complex anthocyan group, which is known to be present in the rind of the cane. The colouring matter was very soluble in water, but when the solution was evaporated to dryness it proved to be insoluble in chloroform, ether, alcohol-ether, alcohol, or methyl alcohol, and was different in many ways from anthocyan. The residue was heated with concentrated hydrochloric acid, and then with concentrated caustic soda in order to destroy any traces of carbohydrates which might have been present. What was left proved to be largely a copper salt, which seems to have been transformed by the sodium hydroxide into some soluble alk-oxide or protein compound. The original colour was doubtless due to this copper compound, together with possibly a small amount of an unknown natural indicator. There was not enough of the substances to permit of an extensive investigation, but the high colouring power may not be without significance in white sugar manufacture.

Comparatively little work has been done on the syrup precipitate. Prinsen-Geerligs gives an analysis of it in his book on cane sugar. ("Cane Sugar and its Manufacture," 1909, p. 211). Geerligs concludes that the precipitate is practically identical in composition with the scale from different evaporating vessels, and that it can not be removed by filtration owing to its gummy nature. On comparing the analyses of the precipitates from Factories Nos. 1 and 2 it was noticed that they were quite different from each other and from that analysed by Geerligs, who found but 27 per cent silica. Here the silica ran 75 per cent and 54 per cent. The character of the precipitate clearly differs as the method of clarification differs. With the sulphitation method as practised in Louisiana it was found quite possible to filter the syrup on a large scale. If a little kieselguhr was thrown into the press first so as to coat the cloths the precipitate could be washed from the cloths without much difficulty and a leaf press working with a head of about 6 ft. give a perfectly bright filtrate. But even when working under most advantageous conditions the process proved expensive, and was frequently omitted when there was any pressure upon the filtering capacity of the house. Numerous experiments were made with a view to improving the filtering quality of the precipitate, mainly by the addition of phosphoric acid or a phosphate in order to precipitate the calcium salts. The factory practice showed no particular improvement under this procedure, which may be readily understood by noting the composition of precipitate (Table IV.). Here the filtered syrup stood for several days at about 12° before it was heated on the water bath, but when heated there was a heavy precipitate of tricalcium phosphate and silicic acid. Clearly these substances, though insoluble in the ordinary sense, were held possibly in colloidal solution by the heavy syrup. This being the case, the addition of phosphates can not be expected to bring down the theoretical amount of calcium in the short time available in factory practice.

In Factory No. 1, using no phosphates, the precipitate was essentially 40 per cent organic matter, 30 per cent silica, the remainder being calcium phosphate, copper, iron, and aluminium salts. In Factory No. 2, using phosphates, the precipitate was 25 per cent organic matter, 30 per cent silica, 25 per cent calcium phosphate, the remainder being copper, iron, and aluminium salts. The copper seems to have been completely precipitated from the syrup.

The organic matter present in the precipitate does not yield reducing sugars by hydrolysis, and is probably mainly a calcium salt of organic acids.

Taking into account the exceedingly small weight of the syrup precipitate, in spite of its apparent volume, and considering also the fact that nothing in the precipitate would affect materially the finished product, the practice of filtering the syrup would hardly seem to do sufficient good to warrant the increased expense. The best procedure is to allow the hot syrup to settle for at least four hours, and as the precipitate forms most completely and settles most quickly at high temperatures, it is as well to have the settling tanks sheathed to prevent radiation as far as possible. The clear syrup can be decanted and the bottoms run back to the limed juice, where the amount of the precipitate is not sufficient to interfere with the subsequent bag filtration.—*Journal of Industrial and Engineering Chemistry*, viii., No. 9.

BRITISH SANDS SUITABLE FOR GLASS-MAKING.[*]

By P. G. H. BOSWELL, H. F. HARWOOD, and A. A. ELDRIDGE.

A SAND composed of grains of one grade, which should not be a coarse one, yields the best material for glass-making, provided that its chemical composition is satisfactory. The silica content must be high, and the quantity of iron oxide present should be less than 1 per cent—the higher limit being permissible only for glass used in making the cheapest kind of bottles. A sand used in the manufacture of the best varieties of glass (optical glass, flint and sheet glass, &c.) should not contain more than 0·08 per cent of iron oxide. Alumina, magnesia, and lime may be present as felspars, ferro magnesian and lime-bearing minerals, and calcareous cement, but are required only for certain glasses; these bases are refractory and lengthen the time required for melting. Sands free from them are preferable, and it is better to rely on the sand only as a source of pure silica, and to add other bases for the purpose of making various kinds of glass. The sand should consist of angular grains. Fontainebleau sand and Lippe (Germany) sand are the most perfect sands for glass-making, and a sand equal in all respects to these does not appear to exist in the British Isles. Sand from Aylesbury, in Buckinghamshire, is, however, practically equal in quality to Fontainebleau sand, but is of less extent; sands from Huttons Ambo and Burythorpe, Yorkshire, and other places, are as good as the Belgian sand

Percentages.

	SiO_2	Al_2O_3.	Fe_2O_3.	CaO.	Loss on ignition.
Lippe	99·88	0·18	None	None	0·21
Fontainebleau..	99·80	0·13	0·006	Trace	0·18
Belgian	99·38	0·30	0·02	None	0·23
Dutch	99·23	0·50	0·02	None	0·22
Sandymount Strand, Dublin..	84·24	3·61	0·47	4·65	4·81
Jura, shore-sand	97·89	1·19	0·07	0·18	0·42
Parsley Hay, High Peak	74·54	18·04	0·05	0·19	7·24
Brassington, High Peak.	90·40	6·56	0·18	0·16	2·48
Abergele	99·35	0·54	0·04	None	0·36
Charlton, Thanet Beds..	95·21	2·43	0·42	0·19	0·88
Alum Bay, Headon Hill Sands	96·96	1·90	0·11	0·34	0·64
Aylesbury, Lower Greensand	99·80	0·32	0·03	None	0·22
Leighton Buzzard, Lower Greensand	99·59	0·25	0·21	None	0·27
Reigate, Lower Greensand	98·93	0·67	0·02	Trace	0·28
Aylesford, Lower Greensand	99·06	0·56	0·04	0·17	0·22
Lynn, Lower Greensand	99·23	0·59	0·04	0·11	0·25
Flitwich, Lower Greensand	98·30	0·87	0·18	None	0·47
Godstone, Lower Greensand	99·56	0·26	0·06	None	0·24
Burythorpe Fox Cover Pit, Helloway Beds ..	96·79	1·63	0·22	None	0·60
Burythorpe Park, Helloway Beds	97·73	1·41	0·06	Trace	0·32
South Cave, Helloway Beds	94·80	2·93	0·13	0·14	0·47
Huttons Ambo, Upper Estuarine	99·04	0·84	0·03	0·10	0·19
Gurseley, Coal Measures	97·45	1·76	0·09	0·13	0·78
Crofthead, carboniferous	97·00	2·02	0·20	0·14	0·76
Muckish Mountain, Dalradian	99·37	0·36	0·05	None	0·12

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[*] Memoir published at the instruction of the Ministry of Munitions of War, by the Imperial College of Science and Technology, 1916, pp. 1-92, with plates and micro-photographs.

imported. The best Lynn sand is also equal to much of the Belgian sand and is superior to some of the Dutch sand. The same applies to Godstone and Reigate sands, but these deposits are irregular. A large number of British sands are less pure, but are well suited to the making of common bottle-glass.

Sands may be improved by washing, burning, extraction with hydrochloric acid, magnetic separation treatment, and grinding, but these operations entail expense, and can only be adopted for sands used in making the best kinds of glass.

Analyses of glass-making sands are given in the accompanying table.

Mechanical analyses of the best sands indicate that a sand for use in glass-making should have at least 70 per cent—and, if possible, more than 90 per cent—of its grains of one grade, and that this grade should be in most cases medium sand, *i.e.*, with a diameter between 0·25 and 0·5 mm.; if the main grade has a diameter of 0·1 to 0·25 mm. so much the better, but such sands are not abundant in the British Isles.—*The Analyst*, xlii., 313.

PROCEEDINGS OF SOCIETIES.

THE FEDERATION OF BRITISH INDUSTRIES.

The Annual Meeting of the Federation of British Industries took place on October 19, 1917, over 400 representatives being present.

The retiring President, Mr. F. Dudley Docker, C.B., gave an interesting address showing what the Federation has accomplished in the first year of its existence. The membership and funds have both steadily increased in a most gratifying way, and the Federation will undoubtedly prove a power for good in the welfare of the empire. At the beginning of the address Mr. Docker gave his reason for refusing an invitation by the Executive Council to remain in office another year. He believes that, to maintain its usefulness, the Federation must be, above all things, progressive, and his view is that to have a permanent President is the first step towards stagnation. Complaints have been made that the Federation has not taken up some special subjects or made pronouncements upon questions engaging the attention of the general public, but the President pointed out that the Executive Committee has been doing most useful spade-work and making careful enquiries, but believes that it is most important to preserve a due sense of responsibility, and to refrain from embarking lightly upon any project, avoiding subjects of secondary importance. The question of the protection of our trade against foreign aggression is one of absorbing interest to manufacturers, and it requires very careful consideration. Mr. Docker believes that it is absolutely essential that we should have the power to bargain with foreign nations, and that the Government must be consulted as to the best method of employing a tariff for the purpose. He is very anxious that the Federation should keep free of alliance with any political party, while being ready to support the Federation in advocating the imposition of a duty upon any article if this action is taken in the interests of British trade, and not at the request or instigation of any politician.

The relation of education to industry was another subject upon which the retiring President had most instructive comments to make. His opinion is that one of the causes of industrial unrest is the lack of knowledge, and he urges that the Federation should show liberality in furthering the spread of education.

The Federation has obtained recognition from the Government, and the Prime Minister has announced that he would welcome any federation of industry, and that he believes that such an Association would be of assistance to any Government. The President hopes that it will ultimately obtain some recognition and status in the eye of the law which would place it in as favourable a position as the Trades Unions.

After the Presidential Address, the meeting proceeded to the election of Sir Richard Vassar-Smith as President for the coming year, and the Vice-Presidents were also elected, namely Sir Vincent Caillard, Lord Aberconway, Mr. A. H. Dixon, Sir Algernon Firth, Sir Robert Hadfield, Mr. W. Peter Rylands, and Mr. Dudley Docker.

In order that the scheme of the Executive Council now in course of preparation might be completed, the present Council was asked to retain office for a further period of three months, and Sir Vincent Caillard was unanimously re-elected Treasurer for the ensuing year.

MEETINGS FOR THE WEEK

Monday, 5th.—Royal Institution, 5. (General Meeting).
—— Society of Chemical Industry, 8. "Patent Law in Relation to British Chemical Industry," by Dr. F. W. Hay.

Tuesday, 6th.—Röntgen Society, 8.15. Presidential Address. Exhibition of Apparatus and Radiographs.

Wednesday, 7th.—Society of Public Analysts, 8. "The Reductase Test for Milk," by P. S. Arup. "Note on Jets for Burettes," by J. H. Coste. "Analytical Examination of Acorns and Chestnuts," by J. L. Baker and H. F. E. Hulton.
—— Faraday Society, 5.30. General Discussion on "Pyrometers and Pyrometry."

Thursday, 8th.—Royal Society. "Structure, Evolution, and Origin of the Amphibia—Part I., The 'Orders' Rachitomi and Stereospondyli," by D. M. S. Watson. "The Enzymes concerned in the Decomposition of Glucose and Mannitol by *Bacillus Coli communis*; Part II., Experiments of Short Duration with an Emulsion of the Organisms; Part III., Various Phases in the Decomposition of Glucose by an Emulsion of the Organisms," by E. C. Grey.

To comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

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THE CHEMICAL NEWS

Vol. CXVI., No. 3024

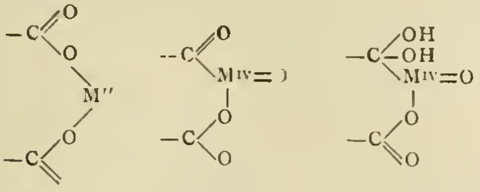
PROBLEMS BEARING ON RESIDUAL AFFINITY.*

By SPENCER U. PICKERING, M.A., F.R.S.

The great majority of known inorganic compounds cannot be represented without attributing to the constituent atoms valency values higher than those commonly ascribed to them. The combination of molecules with each other is sufficient proof that the atoms composing them must possess residual affinity, and therefore additional combining capacity; for the properties of any mass of matter can only be those of its constituent particles. The residual affinity of an atom, A, may be insufficient to attach to it more than one atom, B, but might suffice for the attachment of another B atom if this were already combined, and had only residual affinity available; hence the higher valencies can be expected to come into play only in the formation of complex or molecular compounds, the constituents of which will be united with comparative feebleness.

Oxygen in water, nitrogen in ammonia, and sulphur are conspicuous in forming molecular compounds, and also in polymerising, as is shown by the phenomenal magnitude of the heat absorbed by them on rise of temperature or change of state. On the other hand, carbon and hydrogen appear to have little or no residual affinity, and hence have fixed valency values. As a consequence, compounds of these two elements can be built up in a way that is impossible in other cases. This is also the reason why the substitution of CH_3 for H in an organic compound, or of any other single atom such as Cl or O, evolves practically a constant amount of heat, whereas the introduction of a second Cl or O, since it admits of the residual affinity of the two atoms coming into play, results in a larger heat development.

The metallo-compounds investigated by the author necessitate higher valency values for many metals than those generally exhibited by them. They are isomers of the normal organic salts, the metallic atoms forming part of the anion, being unrecognisable by the ordinary tests, and being therefore directly united to the carbon:—



They are obtained as emulsions, either by double decomposition or by adding alcohol to a freshly prepared solution of the compounds. They are much more soluble than the corresponding normal salts, and gradually change more or less completely into the latter, with, in some cases, a considerable alteration in colour intensity. In cases where the change is not too rapid they may be obtained as scales or glass on evaporating their solutions. Overy forty pairs of such isomers have been obtained containing thirteen different metals, and five different acids; whilst the colour intensity of the copper salts of other organic acids renders it practically certain that similar isomers must exist in all such cases.

Their preparation by double decomposition with the organic salts of sodium implies that these too must exist as such in solution, and the sodi-tartrate and sodi-citrate they have been isolated in scale form.

Alkalis or metallic oxides may take the place of the H_2O in the hydrated metallo salt, and many such compounds have been isolated, some of them being isomeric with ordinary basic salts, from which, however, they differ by being soluble. But the oxygen atom may be displaced by any basic radicle, hence a salt or an acid may combine with a metallo-compound, M_2R'' or H_2R'', taking the place of H_2O; such compounds may be termed metallato-compounds; *e.g.*, sulphato, carbonato-, &c.; many of the cupricarbonates originally isolated were carbonato-cupricarbonates. If the basic and acid radicle in the salt combining with the metallo-compound are the same as those in metallo-compound itself, the product will be isomeric with the simple metallo-compound, and also with the normal salt.

Metallato-compounds are intermediate in solubility between these two; they form jellies or gelatinous precipitates, consisting of minute membranous particles. The formation of them constitutes one of the four or five stages (some of which are often unrecognisable) occurring in double decomposition. When barium chloride is added to concentrated potassium tartrate solution, an emulsion of the bari-tartrate is first precipitated; this rapidly redissolves forming an ato-compound with the potassium tartrate present, its formula being BaT,K_2T; then a bulky precipitate of the ato-compound, BaT,BaT, forms, which after several hours begins to redissolve, and the crystalline normal salt separates from the liquid. With the citrate more than one mixed ato-compound, $Ba_3Cit_2x(K_3Cit)$, is produced, some of which are sparingly soluble.

Such metallato-compounds, since they contain the group OK, not derived from an acid hydroxyl, must be alkaline, and it is owing to their presence in solutions of organic salts that these are alkaline. Such alkalinity cannot be explained by hydrolysis, for it is found that litmus is equally sensitive to acids and alkalis, and hydrolysis would liberate equivalent proportions of each.

The neutralisation of an alkali by an acid is but a special instance of double decomposition, and follows the course indicated above, but the ato-compound formed, instead of being alkaline, will be neutral, except for a slight acidity due to partial hydrolysis. Definite compounds with acids have been isolated in several cases where the metal was one of the metals of the alkaline earths, and where it was one of the alkali metals proof of their existence has been obtained by acidimetric methods. It is owing to the formation of these neutral compounds of acids with organic salts that exact titration of organic acids is generally impossible. The proportion of acid combining with the salt in solutions of decinormal strength varies from 0·3 to nearly 4 equivalent. A curious result of such combination is that the presence of potassium citrate, &c., prevents the evolution of carbon dioxide when an acid is added to a carbonate.

Ato compounds containing different acid radicles have been investigated. Evidence as to the existence of $2K_3Cit,3(K_2SO_4)$ has been obtained, and it is owing to the formation of this (or analogous compounds) that the presence of an organic salt interferes with the determination of sulphuric acid, barium, &c., by precipitation. A barium salt added to the above compound results in the formation of a small quantity of a gelatinous or membranous precipitate, which is evidently an ato-compound, but contains only the elements of barium sulphate, and must be sulphato-sulphate. Other evidence as to the possibility of inorganic salts existing in the metallo condition has been obtained.

With organic compounds acidity is dependent on the presence of hydroxyl side by side with a doubly-linked oxygen. It is inconceivable that a constitution which is essential in this case should not be essential in any other; it is equally inconceivable that this doubly-linked oxygen, if essential to acidity, should play no part in neutralisation. The acidity of the haloid acids is known to depend on the presence of water; to admit of the true acid containing the group XOOH, the elements two molecules of water must be present, and, as a result, the halogens must be heptads, a value already assigned to them on other grounds. Similarly, sulphur, &c., will sometimes have to be octads, and phosphorus, &c., nonads. That a doubly-linked of oxygen is present in all acids seems to be proved by the fact that all the so-called neutral salts of the alkali metals, and of the metals of the alkaline earths, are really alkaline, just as are the salts of organic acids, though in a much feebler degree; the same explanation must apply in both cases, and this involves the presence of some of the salt in the form of a metallato-compound, and hence the presence of $X=O$. The alkalinity of these salts is independent of the method of preparation and purification, and is of the order of 5×10^{-4} MOH for a grm.-equivalent of the salt.

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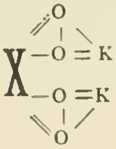
* From a paper read before the Royal Society.

Since carbon is incapable of assuming a valency higher than 4, carbonic acid can be monobasic only; the supposed dibasic acid, H_2CO_3, is unknown, and the compounds derived from it have certainly no claim to be considered as true salts—the product of the *neutralisation* of the acid by an alkali—for with alkali metals they are strongly alkaline, and the heat of their formation is much below the normal. All the other seven cases in which the heat of neutralisation is abnormally low are similar. Ortho-phosphoric and arsenic acids must be dibasic only, unless we assign an unacceptably high valency value to phosphorus and arsenic, and the heat of neutralisation shows them to be dibasic, the displacement of the first two hydrogen atoms evolving the normal amount of heat, whereas that of the third evolves little more than half this quantity, and the resulting products are strongly alkaline.

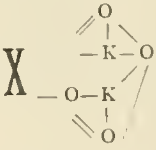
The accepted neutralisation equation—

$$XOH + HOM = XOM + HOH$$

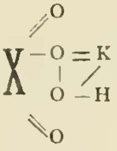
represents a case of double decomposition, which should therefore be reversible, and in which the heat evolution should be 8900 cal. (the heat of condensation of a molecule of water), since the chemical interchange of atoms from combination with one oxygen atom to combination with another should evolve no heat. The fact that the actual evolution is 13743 cal. shows that some affinity not represented by the equation must become satisfied. This must be the residual affinity of the doubly-linked oxygen atom, which comes into play on the substitution of hydrogen, which possesses no residual affinity, by a metal which possesses such affinity. With these affinities operating, a normal salt of a dibasic acid will be represented by I.,—



I.



II.



III.

and the corresponding metallo-compound by II.; this latter, as will be seen, is now represented as the less saturated compound of the two, which it evidently is, since it changes spontaneously into the normal salt; this agrees also with the heat of neutralisation values, for in the case of organic acids, where the metallo-compounds are the main products, the values are 2 per cent lower than with inorganic acid. Another remarkable feature of the heat of neutralisation, which is quite inexplicable on the dissociation theory, is explained by these views, namely, that the total heat of neutralisation of dibasic inorganic acids is normal, but that the addition of the first equivalent of base develops 18 per cent more heat than that of the second. Formula III. shows that the acid salt need not be, as it thus certainly is not, intermediate between the neutral salt and the acid. But with organic acids the heat developed on adding successive equivalents of base should be, and is, almost constant, for no acid salt is formed; the first equivalent of base produces the metallo-compound, which unites with the rest of the acid left to form the neutral metallato-compound, and the second equivalent converts the acid in this into the normal salt, this remaining combined with the metallo-compound in the form of the slightly alkaline metallato-compound.

In many cases there is a development of heat, often considerable, on adding alkali in excess of that required to saturate an acid, and the combination of alkali with normal salts have further been established by alkalimetric methods; the combination results from the conversion of $MO-X=O$ into $MO-X=(OK)_2$, analogues of basic salts. Taking the difference between the heat of neutralisation of inorganic and organic acids as being due to the fact that the normal salt is almost the sole products in the former case, and the metallato-compound in the latter, a rough estimate may be obtained of the heat developed in satisfying the residual affinities concerned, and, applying this to Formula I., the value for the normal heat of neutralisation should be 12419 cal., which is in quite as good agreement with the observed value of 13743 as could be expected under the circumstances.

THE GREAT FOOD PROBLEM.

Clean Culture Farming. Bread from Stones.

By SAMPSON MORGAN.

Bread from stones the farmers will ask incredulously? But why not? Have I not shown from my articles that it is possible to get it? And this bread will be perfect because it will be made from perfect grain. Granite dust according to recent experiments, inspired by my clean culture propaganda, increases the fluorine and phosphorus contents of roots, fruits, and particularly of wheat grains. This fact alone must eventually induce the legislature to make the use of granite dust by wheat growers compulsory. Perfect health of body and mind without the highest percentage of both these non-metallic elements in foodstuffs is impossible. Fluorine is of the utmost importance for bone, hair, and nails. The percentage of phosphorus is higher in wheat grains than in any other vegetable product. Phosphorus—the great brain, nerve, and health food—is higher in wheat grains, or whole wheat meal grown under clean culture granite dust fertilisation, than in wheat grains, or wheat meal grown under any other form of feeding.

"Without phosphorus no thought." As the phosphorus in the brain is derived from the blood, and the blood from the diet, the importance of my clean culture food reform movement is perceptible to everyone. With a knowledge of the agricultural districts all must see that the time has come when the whole industry should be completely changed and put upon a modern business basis. If the present type of farmer cannot effect the transformation then a better class of cultivator must take his place. The existence of the people depends to a very great extent upon the proper development of the food resources of the nation's acres.

We import over 10,000,000 tons of cereals, and raise about 6,500,000 tons. Yet less than one-third of the 16,500,000 tons of grain are eaten by the people. The live stock in the fields are eating us out of house and home. No wonder the representatives of Japanese agriculture who saw our boundless ranges of pastures and hordes of cattle should be astonished, because the simple British people allowed the bulk of the grains they imported and grew to be given to live stock.

The belief that flesh is necessary for health and strength is a very costly one, to say the least.

One acre of land in England will support two men. According to one estimate in China it will support twelve, while in another it is claimed that it will support twenty. There the farmer looks upon labour as the basis of all success. I have often insisted that if the land of Britain was properly tilled it would feed 100,000,000 people. One enthusiast states that if it was cultivated as is the soil in China it would feed a population of over 500,000,000. True China has a superior climate and so on, which our enthusiastic friend omitted to emphasise; nevertheless the above figures are sufficient to stimulate thought.

In 1653 Captain Walter Blith published a book on agriculture, which he addressed to Lord Cromwell and others, in one chapter of which he says, "Tillage yieldeth the greatest profit." Jethro Tull, of 17th century fame, was a persistent advocate of tillage, putting it before everything else in farm work, having years before he began to experiment on the land observed that the vine growers used little or no manure because it affected the flavour of the wines. On the Continent he learned the importance of tillering in vine culture, and he concluded that, as it improved the vine, so it would improve wheat and other crops. He was a firm believer in the importance of allowing the air into the pores of the soil as well as the moisture from the atmosphere. Aeration, ample space for each plant, and free hoeings during the season of growth he considered vital, and finally he used no manure whatever, depending upon persistent cultivation alone. During fourteen consecutive years in this way he obtained from 30 to 36 bushels of wheat an acre and upwards, the last crop being greater than the first. Cobbett when he visited Tull's farm said it was one of the finest sights he had ever seen, and Cobbett knew what he was talking about in this connection.

Wheat 100 Bushels an Acre.

General Cotton, who was prominent in the days of the old London *Echo*, when I was initiating the fruit growing and fruit eating movements in its columns, claimed to have grown wheat at the rate of 100 bushels an acre—the present acre average is 33. He obtained this remarkable result by deep digging, aeration of soil, and hand planting the wheat grains one and a quarter feet each way. The average yield per plant was 55 ears. An acre thus dealt with would contain nearly 30,000 plants. He summed up the situation by saying, "It is simply giving more air to the soil," and he was right. He grew and exhibited a plant of wheat 6 feet high having 65 ears.

Scientists tell us that of every 100 parts of the wheat crop 95 per cent is derived from air, sunlight, and moisture. In 50 tons of manure there are 40 tons of water. In the residue there is only the most infinitesimal part that can be claimed as worth anything. Manure being a soil sourer and poisoner, as I have shown, its use is as unjustifiable as it is costly.

In experiments some years ago under-drainage alone increased the yield of oats from 30 to 40 bushels an acre, the extra weight of grain alone being 400 lbs. Deep ploughing with green manuring alone assured a yield of 40 bushels of wheat against 30 bushels of oats, and an increase of 650 lbs. of grain to the acre.

It has also been found, as one would naturally expect, that sub-soils contain on an average 30 per cent more of the inorganic elements of plant food than the surface soils and when these soils were dealt with by spade labour the yield from the surface soils was seventeen-fold, and from the sub-soils forty-fold. This was greatly due to deep digging, increased sub-soil aeration, &c., enhancing the supply of available mineral matter, of which the shallow surface soils had been depleted. "I was greatly astonished many years ago," wrote an agricultural reformer, "when I dug up an average of 14 lbs. of potatoes per root, planted 3 feet apart each way, in a rich sandy soil at Tunbridge Wells, equal to 30 tons an acre, simply through aerating the sub-soil by a three-feet deep digging." But with the bonfire ash fertilisation alone I lifted plants bearing 35 fine potatoes to a root, at the rate of over 50 tons an acre.

The farmers cannot by deluging the land with manure make up for lack of cultivation, and that the agriculturists of the sixteenth century knew better than do those of the twentieth century.

The national acre average for potatoes is seven tons. It could be made ten easily by the aid of granite and ash. In addition, instead of decreasing the output by a loss of 2,000,000 tons through disease, why should the loss not be turned into a gain by the aid of scientific cultivation. In this way a total wastage of over 5,000,000 tons could be prevented.

There is no reason why the acre average for wheat should not be 10 bushels more than it is. On 2,225,000 acres devoted to that crop the annual wastage exceeds 22,000,000 bushels of bread making grain. Yet legislators have made it a criminal offence to throw the bread crumbs which fall from the table to the birds.

Near where I write a gentleman farmer with labourers of fifty years' experience in farm work has recently deluged land intended for wheat with manure. As a matter of fact every hour spent upon the labour entailed was worse than wasted. The pea crop which preceded the wheat was a most miserable one, and it was grown in a broken up pasture, and that also had been deluged with manure previous to sowing. Every hour also spent in carting and distributing that manure was also wasted. These facts are evident to anyone acquainted with the most elementary principles of soil science.

The broken up pasture with the addition of mineral in the form of ash preferably or of granite dust would have contained ample plant food for peas. The wheat needed nothing but granite dust and gypsum, or a bland form of lime with the former dust. This is but one of thousands of cases in which the land is imperfectly and wastefully treated. Despite all the talk about economy as a nation we do not know what frugality really means. In respect to food production the ordinary agriculturists, from the highest official down to the humblest farmer, appear banded together for the purpose of maintaining methods which are discreditable to the age in which we live. Whilst manufactures have progressed agriculture lags in the rear, and there are actually numerous centres where the lazy methods of the Tudor age are still perpetuated.

I could refer to broad expanses of pastures where nothing whatever in the form of mineral plant food has been added possibly for fifty years. There are millions of such acres with their restricted output, an output which is shameful, held by cultivators who are totally unacquainted with a smattering even of soil science, and who are content to jog along on the old lines, devoting their impoverished pastures to low-grade stock, which in hard winters, like the soil they feed upon, are half starved.

It is time the owners and farmers of these run down lands were called to account, and compelled to take a leaf out of the book of progressive and prosperous city industrial concerns.

Miles and miles of these impoverished acres cry out aloud for phosphates, for dust of the vitalising primitive rocks with their fertilising electrical influences, of which the sour and sluggish soil stands so greatly in need.

Amongst the conclusions formed from investigations in the production of food it was admitted that well tilled arable land will supply twenty-seven times as much human food as is now produced by our poorest pastures. And yet year after year the huge loss of foodstuffs through this slovenly system is repeated without any attempt being made by the Government to stop it.

Though I use the term "poorest pastures" I would emphasise the fact that they are poor not because of the nature of the soil but because of lack of mineral plant food and cultivation.

With a great food shortage confronting us it is nothing less than criminal, that with our costly Department of Agriculture and a bulky and highly paid staff of officials, these lamentable conditions have been allowed to rule ever since the time when the first Minister of Agriculture was appointed.

It is actually suggested that the annual average production of meat from poor pastures is only 20 lbs. per acre, though such land put under the plough could be made to produce an average of 15 tons of potatoes or of 40 bushels of wheat an acre. With the perpetuation of such methods the wonder is not that the four-pound loaf has been up to a shilling, but that the people have not been brought face to face with actual famine.

Ten Million Extra Acres Needed.

From the first day of the war I have persistently emphasised the necessity for taking 10,000,000 of the 17,000,000 acres of permanent pastures, in which millions of acres of the "poorest pastures" I have mentioned are included, and putting two-thirds of them mainly under wheat and potatoes. Year after year that suggestion has been ignored until this year the Government was compelled by the sheer force of circumstances to do something, and at last they have decided to increase the wheat areas by 3,000,000 acres, and then only next year. The 10,000,000 extra acres I have proved were absolutely necessary should be devoted to wheat, oats, barley, and potatoes.

Under clean culture the pastures, after being broken up with simple dressings of fine dust of the primary rocks and gypsum, or a bland form of lime, would be perfectly fitted to assure bumper harvests of wheat, and of wheat of far higher nutrient quality than any now upon the markets of the United Kingdom. Thus these extra lands could have been dressed to perfection, economically, and with the lowest possible expenditure upon labour. With regard to labour there is ample available. A staff of sturdy farm-hands have been engaged for weeks near where I write, tarring the highways to make motoring more delightful—at such a time too?

The official experts in fertilisation have been recently expressing doubts as to the possibility of farmers getting the necessary supplies of potassic fertilisers. Well, there are the granite rocks about us on every hand, and they contain the very material that they complain may not be available.

Nothing but the primitive rocks alone, ground down without any treatment for the production of extracts of a costly nature, are necessary, and such can be had now in abundance for perfectly fertilising wheat, barley, oats, and potato crops to perfection. It can even be supplied to the wheat that has already been sown this autumn after the plants are up.

The provision of this powdered felspar will prove one of the greatest boons ever conferred upon agriculture. With it the whole of our run down and impoverished pastures, together with our grain and potato lands, can be well fed, cheaply and easily. In this way the whole of the community next year would enjoy greatly increased supplies of perfect foodstuffs at pre-war prices. Had this method been adopted at the outbreak of hostilities these cheap and abundant supplies would have been enjoyed without a penny rise in the market price of any of them. We could have had the full weight, four pound pure wheaten loaf at sixpence so long as the war should last. The war has proved that our official departments have failed us lamentably all round. And why? Because they are staffed with political nominees and not with the best brains obtainable.

We are a nation of spendthrifts so far as agriculture is concerned. In addition to the granite rocks, solidified bonfire ash, there are millions of tons of splendid fertilising material in the dust of burned clay about the brick kilns throughout the four kingdoms. At one brick works I saw immense quantities of this material in heaps covered over with luxuriant weeds. Yet it forms a splendid and true mineral plant food for the crops I have mentioned, and for fruit of all kinds it is invaluable. I could name one large commercial producer who, by its aid, has made from £50 to £150 per acre from pears.

In my speech at the opening of the Swanley Horticultural College, which I founded, I exhibited some of these pears, and they were so large and richly coloured that I heard one well known gardening editor whisper to another at his side, "They are foreign." But they were home-grown. Every authority on roses commends manure. But it is the very worst material for the purpose. It induces weak shoot growth, and this in time becomes smothered with aphides, thanks to the manure.

It is easy to get sturdy rose bushes smothered with the largest, cleanest, and most fragrant flowers each year by reliance solely upon wood ashes, brick-dust, or granite dust. All these materials are perfect for grain, fruit, and flower production on clean culture lines. They will double the saccharine content of sugar-beets, mangolds, and similar roots. Through neglectful cultivation of the broad acres of Britain we are losing millions of money each year, some of which should go into the pockets of the producers, distributors, and landowners, and a goodly part into the National Exchequer,

The politicians have been saying almost daily that we must economise. But what about the continuance of this National waste for neglecting to control which they alone are responsible? We are losing millions of tons of good food also, and yet with the most serious of faces we are continually saying, "We must economise." What sarcasm! Why do we not make a start with the land and make it produce the whole of the grain needed for our daily bread?

CHEMICAL NOTES.*

New Lead Corroding Process.

The pig lead is weighed as required for corrosion; then run over a travelling crane to the melting furnace. This furnace has a capacity of five tons, and is heated by gas. From the furnace the molten metal is poured through a patent wire making machine, from which the lead emerges in the form of wire, granulation being avoided by keeping the wires at a red heat. The wire produced in this form retains its porous condition even under weight in the corroding vats. From this machine the lead in wire form is conveyed by travelling belt to boxes, which in turn are trucked to the incline hoist, from which they are automatically dumped into the corroding vats over planks which distribute the load and prevent its consolidation at any one point. This process is repeated from time to time as corrosion progresses.

Corrosion is effected by a weak solution of acetic acid. The corrosion vats are set on an incline, one below the other so that the solution is syphoned from one vat to the other and kept in constant circulation, the content of the bottom vat being re-pumped back to the top of the series.

These vats are 7 ft. 6 in. in diameter, and hold a ton and a half each of lead and solution. They are made of California red wood, which does not stain the solution. The vats are fitted with false bottoms, The bottom vats are covered to ensure cleanliness and avoid evaporation of the acid. The bottom vat is 10 ft. by 6 ft., and the solution is retained here till it becomes sufficiently dense as shown by test hydrometer readings. The solution is then pumped to the precipitation vat where it is treated with carbon dioxide produced from lime rock and coke, the gas being injected by a blower pump. The gas is purified before use by being passed through a scrubber and water-spray filter, which free it from tar, &c.

From the bottom of the precipitation vat the precipitate is drawn off into the washing vats, of which there are three. The acetic acid is recovered and used over and over again. From the washing vats the precipitate is pumped to the filter press, which has a capacity of 5 tons for each eight hours. The frames and plates are made of acid resisting yellow pine.

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* Abstracts reprinted from the *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, May, 1917.

From the filter press the white lead is taken, in the form of cakes, and loaded into boxes in which it is conveyed to the drying room. After drying it is disintegrated by passing through wooden rolls and placed in barrels.

The process is remarkable for its efficiency and the exceptionally high quality of the white lead produced by it.—*Mining and Engineering Record*, Oct. 1916, p. 101.

Technological chemical Research on Superphosphates.

Many samples of superphosphates were examined by the author chemically and with the petrographic microscope, and experiments were made on the conditions of equilibrium of the system, lime, phosphoric acid, and water at 75° C., and at 100° C., and on the influence of various factors on the physical properties of superphosphate. Contrary to the view generally accepted, the calcium sulphate present in superphosphate prepared from mineral phosphates usually exists mainly or entirely as anhydrite; only in rare instances is it present chiefly or solely as the dihydrate. In bone superphosphate, on the other hand, usually prepared with a restricted quantity of sulphuric acid, the dihydrate is present more frequently. Mono- and di calcium phosphates occur usually only in the hydrated form, but the anhydrous salts are also sometimes present. The physical properties of superphosphate depend chiefly on the amount of the liquid phase which is always present. For analytical purposes the liquid phase is defined as the sum of the free water and the free phosphoric acid. To determine these the superphosphate is extracted with cold 95 per cent alcohol, and the residue is washed with a little ether, dried for one hour at 80° C., and weighed; the loss of weight corresponds to the free water plus free phosphoric acid. In the alcoholic solution, after dilution with water, the phosphoric acid is determined either volumetrically or gravimetrically. Results obtained with numerous commercial samples of superphosphates indicate that, in general, the best products in regard to dryness and friability are those in which liquid phase is less than 15 per cent; products containing 15—18 per cent of liquid phase are still dry and friable, those containing 18—25 per cent are slightly moist, and readily cake. In the technical preparation of superphosphate the first stage consists in the reaction of sulphuric acid with part of the tricalcium phosphate to form calcium sulphate and phosphoric acid. In the second phase the free phosphoric acid reacts with a further quantity of the tricalcium phosphate; this reaction proceeds with appreciable velocity only above 50—60° C., and with sufficient velocity for technical purposes only at 70—80° C. As the temperature of reaction increases, the amounts of free water and of free phosphoric acid in the product also increase; hence attempts to improve the physical characters of superphosphate by increasing the temperature of reaction are irrational. The best results will be obtained when the reaction temperature is from 80—100° C., and as the quantity and concentration of the sulphuric acid used in practice may be regarded as fixed, the aim should be to maintain the desired temperature by variation of other factors, such as the dissipation of heat during the process, the total mass of the system, the duration of the mixing process, and the quantity of water evaporated, *e.g.*, by ventilation of the superphosphate dens.—N. Pratolongo, *Journal of the Society of Chemical Industry*, Oct. 31, 1916, p. 1073.

Detection of Nickel in Cobalt Salts.

By the following method considerably smaller quantities of nickel can be detected than has been possible hitherto, and with a smaller consumption of dimethylglyoxime, even in presence of relatively large quantities of cobalt. The solution containing nickel and cobalt (about 10—15 cc.) is treated with 10 per cent potassium cyanide solution until the precipitate which forms at first just redissolves, and the solution is heated and rotated for five minutes after the colour changes from greenish brown to pale yellow. It is then diluted to 50 cc. with water at 85° C., and treated with 1 cc. of a 1 per cent alcoholic solution of dimethylgloxime, after which 1 per cent silver nitrate solution is added, drop by drop, with constant stirring, until a permanent precipitate is produced. The presence of nickel is indicated by a pink colour, which appears only after some hours when the quantity of nickel is very small. It is possible to detect 0·02 mgrm. of Ni in one hour and 0·002 mgrm. in twenty-four hours. The effect of the silver nitrate is to precipitate the cyanide ion as silver cyanide and promote decomposition of the nickelocyanide on, thus increasing the concentration of nickel ions, whilst the cobalticyanide ion remains practically unaffected. The increased sensitiveness of the test is probably due to increased concentration of nickel ions owing to adsorption by the precipitated silver cyanide. A similar effect is produced if silver chloride be precipitated in the mixture, but precipitation of a positive colloid, such as aluminium hydroxide, has no effect.—A. R. Middleton and H. L. Miller, *Journal of the Society of Chemical Industry*, Oct. 16, 1916, p. 1013.

The Texture of Firebricks.

The texture is one of the most important qualities of a firebrick, because if the chemical composition and refractoriness are satisfactory, the characters of the brick will depend on the texture; *i.e.*, on the proportions of coarse and fine grains and the spaces between them. These grains are composed of (*a*) felspathic and micaceous fluxes, (*b*) granules of clay proper, (*c*) grains of quartz, and (*d*) accidental impurities. When a clay is burned in a kiln the fluxes begin to melt at about 900° C., and then attack the surfaces of the clay and quartz grains. At a still higher temperature the clay and quartz react on each other and bind the material together into a solid mass of great strength. This fluxing or vitrification is a time reaction which is favoured by high temperature, by fineness of grain, and by pressure which brings the particles closer together. Consequently, the coarser the grain the higher the softening temperature and the refractoriness. Grog or burned clay, being coarser than raw clay, has a higher softening point, so that the refractoriness of a clay may be raised by adding grog made of the same clay. Coarse-grained materials are less liable to crack when exposed to sudden changes of temperature, but they are mechanically weak and liable to rapid destruction by abrasion or corrosion. To resist the latter, fine-grained materials are essential. They may be less refractory, but true refractoriness is often of secondary importance, and must be sacrificed to secure greater durability under furnace conditions. Machine-made firebricks are commonly regarded as inferior to those made by hand. This is largely due to unfair comparison, the material for the latter being more suitable than that supplied to the machines. Pugged clay is often irregular in texture, and machine-made bricks are frequently manufactured from clay which has not been allowed to stand long enough to mature properly. Uniformity of texture is so essential that its importance cannot be over-emphasised. The texture may be judged by polishing one face of a brick or other article and cementing a glass plate on it by means of hot Canada balsam.—J. W. Mellor, *Journal of the Society of Chemical Industry*, Dec. 15, 1916, p. 1218.

Thermal Conductivity of Materials Employed in Furnace Construction.

The author reviews the work of Wologdine, Marshall, Dougall, Hodsman and Cobb, and B. Dudley, and is dissatisfied with each of their methods. He proposes a method in which ordinary sized specimens (such as firebricks) are heated by immersing one face in a bath of molten metal heated electrically so as to secure a uniform temperature throughout the face to be tested, and a flow calorimeter consisting of numerous turns of piping attached to a water supply of constant temperature and pressure is applied to the cooler face of the specimen. The rate of flow of the water is adjusted to produce an equal temperature rise in equal intervals of time. The temperature of the cooler face of the specimen is measured by means of differential couples of six pairs of copper-constantan immersed in the flowing water. The calorimeter is fitted with a guard ring which is separated from it by a narrow gap about 1 mm. wide filled with mica plates set on edge. This arrangement gave results which agreed with those obtained by placing the hot face of the specimen on an iron plate, which formed one of the walls of a large muffle, and determining the temperature of this face by means of a bare nickel copper-nickel couple cemented into it, but the use of a molten metal bath gave more concordant results. In working with thick samples it is necessary to allow ample time for equilibrium to be attained; this sometimes takes several days. Tests on a brick made of diatomite bonded with a little clay showed that the conductivity in C.G.S. units between 105° and 502° C. rose steadily from 0·000310 to 0·000461. Tests on a slag-wool mat (CaO 48, SiO_2 43 per cent) showed a conductivity between 194 and 476° C. of 0·000191 to 0·000342. The conductivity-temperature graphs of both diatomite and slag wool were straight lines. By the same method the conductivity of a mixture of basic carbonate of magnesium with 15 per cent of asbestos (such as is used for covering steam-pipes) is about 0·00015 between 20° and 350° C. At the latter temperature the carbonate decomposes, and at a dull red heat the mixture falls to a loose powder of double the conductivity.—E. Griffiths, *Journal of the Society of Chemical Industry*, Dec. 15, 1916, p. 1219.

THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

Objects and Policy of the Institute.

Foundation.—The Institute of Chemistry was established in 1877. There were then comparatively few practitioners in chemistry apart from the professors in the universities and colleges; but the colleges were beginning to train chemists, and a number of the young scientific men of that time foresaw the need for founding an institution which should supply a hall-mark for those competent to practise. Their aim was to provide the public with the means of distinguishing those who had been properly trained and found to be competent by an impartial authority.

A nucleus was formed of chemists who had already established their positions, and a Council was elected consisting of representatives of the various branches of the profession (analysts, consultants, government chemists, technologists, and teachers). A scheme of training was formulated and examinations were instituted.

Incorporation by Royal Charter.—In 1885 the Institute was granted a Royal Charter with definite authority to examine, to grant certificates of competency, and to register persons competent to practise. The aims of the Institute as stated in the Charter included the elevation of the profession of consulting and analytical chemistry and the promotion of the efficiency and usefulness of persons practising the same, by compelling the observance of strict rules of membership and by setting up a high standard of scientific and practical efficiency.

Qualifications for Associateship and Fellowship.—The extent of the training and the scope and character of the examinations for membership have been modified from time to time, in order to maintain a standard corresponding to the highest training obtainable at the best institutions in the country.

The method of conducting the examinations, by chemists in practice as well as by professors, has given the examinations a distinctly *practical* rather than an *academical* bias, and has exercised a decided effect on the advancement of higher education in chemical science, especially on the courses of those colleges from which a steady flow of candidates has been maintained.

Candidates for admission to the Associateship are required to produce evidence of having passed an approved preliminary examination, but in special cases the Council consider other evidence of general education.

The training for the Associateship extends over at least four years.

Admission to the *Examination for the Associateship* is open to—

(i.) Candidates who have been systematically trained in a recognised university or college;
(ii.) Candidates who have been trained partly in a recognised university or college and partly under Fellows of the Institute in laboratories or works;
(iii.) Candidates who have obtained university degrees or other recognised diplomas, the examination for A.I.C. being modified in the cases of those who have taken high honours.

The Council also consider on their merits the cases of candidates who are upwards of twenty-seven years of age and have been engaged in the study and practice of chemistry for at least ten years.

Admission to the *Associateship without Examination* is granted—

(i.) In exceptional cases, dependent on the consideration by the Council of the candidate's age, general education, scientific training, possession of a degree with high honours, experience, original work, &c.;
(ii.) As a temporary war measure, in the case of properly trained candidates who have been engaged with the Forces or on work of national importance.

Admission to the Fellowship is open to Associates of three years' standing who have—

(i.) Carried out original research; or
(ii.) Have devised processes or inventions; or
(iii.) Otherwise satisfied the Council that they are possessed of knowledge and ability equivalent to having fulfilled the conditions contained in (i.) and (ii.).

In special cases, candidates who have had considerable experience are examined for the Fellowship without passing through the grade of Associateship.

In exceptional circumstances, candidates who have had considerable experience and attained positions of responsibility may be elected to the Fellowship without examination.

Present Position of the Institute.—The Institute has now a roll of over 1600 Fellows and Associates, including most of the best known British chemists, and of over 350 registered students.

Its history bears evidence of the earnest endeavours of the Council and Members generally towards the organisation of their profession and the maintenance of its efficiency and status.

The Council have taken action successfully on many occasions in upholding the professional interests of chemists where they have been assailed.

The qualifications and examinations of the Institute have received the recognition of the principal Government Departments concerned with chemical appointments, including the Admiralty, the War Office, the Ministry of Munitions, the Government Laboratories, the Board of Agriculture, the Local Government Boards, and the Colonial Office. The Institute has established examinations on lines agreed upon with the Local Government Boards which are accepted under the "Regulations as to Competency of Public Analysts under the Sale of Food and Drugs Acts," and about 96 per cent of these appointments are held by Fellows of the Institute. The Fellowship and Associateship are also officially recognised by many other authorities, both at home and in the Overseas Dominions.

By conferences on professional matters and by the work of the Censors the Institute has fostered among the Members a sense of mutual responsibility in their relations to the public and to one another as professional men. No institution has done more to raise the status of the profession of chemistry which to-day stands higher than ever in the estimation of the general community.

The appointments Register maintained by the Institute provides a means, which is extensively made use of, whereby authorities and employers can obtain the services of chemists, whilst Members and others can be informed of vacanies.

In this connection it should be mentioned that the action of the Institute has effected a marked improvement on the conditions offered for appointments of all kinds involving competence in chemistry. It has declined to take any part in making known vacanies offering unfavourable prospects, and has urged, with success, technical journals not to accept advertisements tending to degrade the professional status of chemists.

The Council of the Institute, moreover, are strongly of opinion that many operations of a scientific nature should be entrusted only to men of high competence, and this view has been constantly urged in connection with the appointment of chemists in industrial undertakings.

The Institute posseses excellent headquarters, with laboratories and library, and its office is available to Members and others requiring information and advice on all matters of interest to chemists.

It is difficult to realise what the position of professional chemists would have been at the present day if such an Institution had not been founded, and no attempt had been made to bring together in one body those who practise in a calling so necessary to the affairs of everyday life and the progress of civilisation.

During the War.—During the war the Institute has been of direct assistance to many Government Departments and sub-departments, the profession, and the public generally. Advice and help with regard to service with the Forces or in other work of national importance have been freely and impartially rendered available to all chemists and students of chemistry, whether or not they have previously had any connection with the Institute. The services rendered by chemists in connection with the war entitle them to claim a greater measure of public recognition and appreciation than has been accorded them in the past.

The Word "Chemist."—It has long been felt by chemists whom the Institute was founded to represent, that they are at a great disadvantage in having no title to distinguish them from pharmacists, and the matter has frequently been the subject of discussion. The Council hold strongly that those who practice chemistry—as distinct from pharmacy—should be uppermost in the minds of the public when the word "chemist" is used, and they are desirous of taking every step possible to effect this change of usage, especially as this country stands alone in applying the title to pharmacists and druggists. With that object in view, representatives of the Institute of Chemistry and of the Pharmaceutical Society of Great Britain have recently held a conference to consider whether there was any possibility of the Pharmaceutical Society being able to assist the Institute to remedy the state of affairs.

Many pharmaceutical chemists prefer to use the word "pharmacist," and the Pharmaceutical Society rather encourages the use of that title. The President of that Society has undertaken to discuss the matter with his Council, and it is anticipated that a statement on the subject, which is rather complicated by certain provisions of the Pharmacy Acts, 1868 and 1908, will be published in the near future.

Towards More Complete Organisation.—Before the war the Council had under consideration steps to be taken towards the more complete organisation of the profession of chemistry by the Institute, and the Regulations for admission to the membership have lately been modified (as shown above) in such a way that no properly trained and competent chemist need remain outside its ranks. Such organisation cannot be entirely satisfactorily effected, however, unless the great body of properly qualified chemists assist the movement; and it is therefore hoped that all well-trained chemists will consider their position in relation to the new Regulations.

The Council would deprecate any lowering of the standard for the Associateship or for the Fellowship of the Institute, particularly as they realise that high aims alone can safeguard the future of British chemistry. The demand is for the best talent obtainable, for strong leaders and genuine co-operation.

The Council of the Institute hope by the lines of policy indicated above to effect more completely the consolidation in one body of properly qualified chemists in all branches of the profession, so that the Institute may not only continue the work it has done in the past, but broaden its activities both in the interests of the profession of chemistry and of the public.

Published by Order of the Council,
Richard B. Pilcher,
Registrar and Secretary.

30, Russell Square, London, W.C. 1.,
November 2, 1917.

THE CHEMICAL EXAMINATION OF NATURAL BRINES.*

By O. R. SWEENEY and JAMES R. WITHROW.

The proper analysis of natural brines has always been important. They are used by chemical manufacturers to make comparisons with a view to reaching decisions as to prospective yields of salt, bromine, and other products. The war-time elevation of the price of bromine from 30 cents to as high as 6.50 dols. per lb., as well as a similar elevation of other products derived from natural brine, has given rise to search for additional sources of these products, and a careful scrutiny of many of the brines encountered in oil, gas, and coal development, and hitherto wasted. As a result many analyses have been made in the last three years as a basis for manufacturing consideration. Some of these were made in the laboratories of manufacturers themselves and some by consulting chemists. Analyses from both sources have come into the hands of the authors as the basis for report upon prospective manufacturing values. We, also, have had occasion to make check or confirmatory analyses.

It early became evident that there was no standard or uniform procedure being followed by the different workers. To this fact may be due a large part of the non-agreement encountered from time to time, though inexperience with this type of analysis is also a factor. Few chemists, even water analysts, are experienced in such a type of work as bromine determination in brine. This may be shown best by citing a report to its president by the laboratory of the chemical company. The letter from the president of one chemical company to another stated :—

"The analysis of the two samples of brine which you sent us has been completed and it was some job. The results are as follows :—

	Well A.	Well B.
Depth (feet)	1200	1200
Diameter (inches)	8	4
Specific gravity of brine..	1·071	1·070
CaO (per cent)	0·69	0·68
Br	0·42	0·22
Halides (as sodium halide)	9·21	9·26
Iodine	None	None"

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* Read before the Industrial Division, Kansas City Meeting of the American Chemical Society, April 12, 1917.

These samples were from a brine whose composition was well known to us. Furthermore, they were on the same property. It will be noticed that they are of the same depth and also the same specific gravity, CaO content, and halide content. Nevertheless, they are reported of different bromine content—a divergence of nearly 100 per cent. Such a divergence would be a very important matter industrially, for one of these wells would give nearly twice the yield of bromine for the same turnover of salt and calcium chloride and at the same fuel cost as the other well. Considering the difficulty of bromine determination, by the usual methods, the infrequency of demand for it and the concordance of all other determinations on these two brines, one is tempted to suspect the accuracy of the bromine determinations. As a matter of fact even the lower value is over twice the bromine content of the field in question as shown by both analyses by various chemists and experience of *all* the plants operating on this particular brine.

Such situations give rise to controversy and discredit analytical chemistry. An examination of the literature for a basis for standard or uniform procedure disclosed no exact one which could be recommended. The procedures described for the examination of "mineral water" are not applicable directly. Certain modifications which our experience has introduced are recorded here. Not all of the procedures described have been exhaustively studied as yet. The purpose of this paper is to make a beginning with the hope that others, who have had experience in this work, will contribute their experiences, or will criticise these procedures. In this way a procedure may be developed which may be accepted as standard. The object is to develop a method which will meet the needs of the manufacturing chemist rather than a method of exhaustive analysis. Brevity and speed of manipulation, with reasonable accuracy, are therefore the requirements.

Analytical Procedures.

Sample.—The sample when pumped from the earth will generally be clear, but on standing it becomes turbid, due to the separation of a brown precipitate. This precipitate is mainly iron, but may contain silica alumina. It is probably caused by oxidation and hydrolysis of ferrous bicarbonate. Generally by the time the sample will have reached the chemist the iron will have separated. The scheme of agitation to suspend the deposit uniformly through the liquid before taking a part for analysis is inaccurate, as experiments have shown. Furthermore, the specific gravity is changed, and this will affect the entire percentage composition. Consideration of this point has led us to conclude that the best procedure would be to collect a sample of about one litre, allow it to oxidise and settle completely, determine the amount of deposit, and then make analyses on the filtered sample. The analysis would not be exactly that of the original brine, but the difference would be very slight, and, since this procedure gives more nearly the thing that the manufacturer wants, it is best to proceed in this manner.

Deposit on Standing (*Aeration*).—The sample of about one litre, which will usually contain some deposit, is allowed to stand, with occasional shaking, and removing of the stopper, for two or three days, or until deposition is complete and the precipitate settles well. The height of the liquid is carefully marked on the outside of the bottle, and the entire sample is then filtered, rejecting the first 100 cc. The precipitate is well washed, ashed, and ignited to constant weight. The bottle is dried and the amount of water which it contained to the mark is determined. With these data the grms. per litre are calculated, using the specific gravity of the filtered sample, and the result recorded as "*Deposit on Aeration.*" The errors will not be large if percentages be calculated, using this figure. Since in the industries all natural brines are exposed to air and allowed to settle before they are further treated this value is just what is wanted by the manufacturer. Further xamination of the precipitate is not necessary. It is a question whether or not it would be fair to assume the precipitate to be iron oxide (Fe_2O_3) and calculate it to, and report it as, ferrous bicarbonate.

Specific Gravity.—The specific gravity is obtained by the Westphal balance, and is taken at 15° C., although perhaps it would be better to use 20° C., since this is more nearly the average temperature. The specific gravity of the fresh brine will be different from that of the sample through which the precipitate is suspended, and this in turn will be different from the filtered sample. On one brine, for example, the specific gravity of the filtered sample was 1·2307, while that of the sample in which the precipitate was suspended was 1·2342. If the chemist could take the specific gravity of the clear brine as soon as pumped from the well it would no doubt be best, from the point of view of the original brine, but this will generally be impractical. Even if the specific gravity could be obtained on the fresh brine there would be some volume change after the precipitate settled, and a small error would be introduced when taking a filtered sample for later analyses. For these reasons, and also because the manufacturer is interested in the *settled* brine, it is believed that the best procedure is to use the filtered, aerated brine, and to determine the specific gravity with a Westphal balance at 15° C. (?). This value is used in calculating percentages.

Total Solids.—Many chemists omit this determination because of its questionable accuracy, but its value in calculating total water content for "evaporation fuel" comparisons makes it important. Brines rich in $CaCl_2$ require a rather high temperature, above 160° C., to expel the water completely. At this temperature the magnesium and calcium salts lose a part of their acid constituents, and a wide range of values will be obtained, depending on the temperature and duration of heating. The total solids can be calculated from the complete analysis, but this value should be checked by the total solids as obtained by evaporation. This point is being studied in this laboratory at the present time, and it is hoped that by a suitable arrangement the volatilised acids may be collected, titrated, and then be added to the residual weight of the total solids. It may be that a weighed excess of some base may be added to retain the acid which is otherwise volatilised. The constituents likely to volatilise are chlorine, bromine, iodine (slight), sulphur trioxide, and carbon dioxide (slight). The total solids are determined in the filtered sample, using 25 cc. portions, and should be reported as *Total Solids by Evaporation.* This gives the manufacturer a basis for a reasonable estimation of the water to be evaporated in working the brine.

Silica.—A 25 cc. portion of the filtered brine is acidulated with 5 cc. of concentrated hydrochloric acid and is evaporated to dryness. It is then dried at 120° C., or higher if necessary, for an hour. Five cc. of hydrochloric acid are then added, the vessel warmed, 20 cc. of water are added, and after warming the whole is filtered and washed free from chlorides. The filtrate is evaporated and treated as just described, and the operation is repeated on the second filtrate. The combined precipitates are ignited in a platinum crucible and weighed. The residue is treated with sulphuric and hydrofluoric acids. The loss in weight is reported as *silica*, and the residue is added to the iron and alumina.

Iron and Aluminium.—The filtrate and washing, which should contain 5 cc. of concentrated hydrochloric acid, are treated with a few drops of nitric acid, boiled a few minutes, and then made alkaline with ammonia. It is then boiled until all the ammonia is expelled, and after standing is filtered, washed, and ignited in the crucible from which the silica was expelled. The residue is reported as *Iron and Aluminium Oxides.* A separation of the iron and aluminium is not necessary. The result should be reported separately from the iron which separated on aeration. It should be remembered that the iron, aluminium, and silica are not in solution as oxides, but as salts. For this reason there will be a slight difference between the total solids on evaporation and the calculated total solids.

Much time is saved if the iron, alumina, and silica are all precipitated together, with ammonia. The amount of silica remaining in solution is very small. These constituents have no commercial value, and need not be reported separately. It should be remembered in this latter case that ammonium clhoride must be added.

Calcium.—The filtrate from the iron and aluminium is diluted to 250 cc. and 25 cc. are taken; this is diluted to 150 cc., heated to boiling, and a hot 10 per cent solution of ammonium oxalate is added in excess. After standing for some time (fifteen minutes) it is filtered and washed with hot water. The precipitate is dissolved in warm dilute hydrochloric acid, a little ammonium oxalate solution added, and ammonia then slowly added to complete the precipitation. The precipitate is filtered out, after standing one-half hour, and is ignited to the oxide and weighed, or is dissolved in dilute sulphuric acid and titrated with permanganate. Our experience seemed to show that it was not necessary to allow the precipitate to stand twelve hours as is recommended in some of the books in water analysis. The calcium should be reported as sulphate and chloride.

Magnesium.—The combined filtrates and washings from the calcium are acidified with hydrochloric acid, a large excess of sodium hydrogen phosphate is added, and then ammonium hydroxide with constant stirring until the liquid smells of ammonia. Ten cc. of strong ammonia are added in excess, and the whole is allowed to stand twelve hours. The precipitate is filtered out, washed with dilute ammonia, and redissolved in hydrochloric acid (1:5). The volume is made up to 77 cc., a little sodium hydrogen phosphate added, and then ammonia drop by drop, with constant stirring until the solution smells strongly. After four hours the magnesium is filtered out on an alundum or Gooch crucible, washed with 2 per cent ammonia water, dried, and ignited to $Mg_2P_2O_7$. If an alundum crucible is used it should be heated within a glazed crucible. The magnesium should be calculated to the bromide and chloride.

The above procedure gave very good results. In the usual procedure the filtrate from calcium is evaporated to dryness, and the ammonium salts are volatilised. This requires great care and much time, and did not give any better results than the procedure described. The reprecipitation must be carried out, even on very small amounts. There seems to be good authority, however, for the evaporation and ignition which we have omitted, and the point should be investigated further. (In the discussion of this paper in the Industrial Division it was suggested that the speedier method for magnesium, used in Low's "Technical Methods of Ore Analysis," p. 159, might be of service here, but we have not yet investigated this method, or the method of precipitation with sodium hydroxide, sometimes used on traces of magnesium).

Barium and Strontium.—If no sulphates are present, barium and strontium must be looked for. Indeed, a case is on record where barium, lead, and sulphuric acid were present simultaneously in a natural mineral water. (Carles, *Ann. Chim. Anal.*, 1902, 91) From work in progress in this laboratory it seems, however, that in this case of brines, where very little CO_2 is present, that sulphates preclude the presence of barium or strontium. Barium oxalate is sparingly soluble, and a strontium oxalate is insoluble in water. When these metals are present they will be partially precipitated along with the calcium. This point seems to have been overlooked hitherto. In cases where the barium and strontium amount to 0·2 per cent the error introduced cannot be neglected. The magnesium results may also be affected. It may be possible to precipitate the barium and strontium with ammonium sulphate before precipitating the calcium, but no work has been done on this phase. The fact that the barium is not completely precipitated by ammonium oxalate makes it impossible to apply a correction to the calcium precipitate. The determination of the barium and strontium in the calcium precipitate is too time-consuming to be practical for the ordinary technical analysis. When the barium and strontium content is small the error can be ignored. The procedure used was identical with the one described in the *Department of Agriculture Bull.* 91, "Mineral Waters of the United States," by J. K. Haywood and B. H. Smith; a simpler method has not yet been found.

Ammonia.—Traces of ammonia have been reported in some brines, but the amount is generally so small as to be of no commercial importance. It may be, however, that its significance is greater than we now know, especially in brines for electrolysis. The suggestion has been made by cell operators that nitrogen chloride may be connected with the explosions which occur from time to time in electrolytic chlorine apparatus. If this should prove true the determination of ammonia will be important.

Sulphuric Acid, Sodium, and Potassium.—Fifty cc. of the filtrate from the iron and alumina are diluted to 100 cc. and treated, while boiling hot, with 10 per cent $BaCl_2$ solution, adding it slowly and with constant stirring. The $BaSO_4$ is filtered off, the paper burnt off in a porcelain crucible, and the precipitate dissolved in a few cc. of warm, concentrated sulphuric acid. The solution is now carefully poured into 250 cc. of water, and, after standing some time, is filtered, washed, and ignited. It should be reported as calcium sulphate. This method of freeing the $BaSO_4$ from iron and other absorbed matter is very effective. It is essentially that taught for decades at the John Harrison Laboratory, University of Pennsylvania, Philadelphia.

The filtrate from the sulphuric acid is used for sodium and potassium. From this point the procedure we have been using is the *same* as described in "Mineral Waters in the United States," *loc. cit.* It is difficult, however, to determine small amounts of potassium in the presence of large amounts of sodium chloride, and it is believed that some procedure should be used which will precipitate most of the sodium first. (Prof. C. W. Foulk, of the Division of Analytical Chemistry of the Ohio State University Laboratory, is now investing this matter).

Chlorine.—The brine should be tested with phenolphthalein. It will usually be neutral, but if it is not it should be made so with $NaHSO_4$ solution. Ten cc. of the filtered sample are diluted to a litre and 10 cc. used for titration. This is diluted to 200 cc., 2 cc. of K_2CrO_4 solution are added and the mixture is titrated to the end-point. Na_2CrO_4 would probably be a satisfactory indicator here, but we have not yet proved this to be true. Take an amount of standard sodium chloride solution equivalent to the amount of silver nitrate used, dilute to 200 cc. and titrate as before. The difference represents the amount necessary to affect the indicator, and should be subtracted. This procedure is accurate enough since *the chlorine is used only as a check on the analytical work.* The bromine value must be deducted.

Bromine.—The colorimetric procedure, as given for ordinary waters, is not usable with brines. Experiments showed that after repeated extraction with 90 per cent alcohol the residue still contained bromine. The distillation methods are time-consuming and not very easily manipulated. For these reasons a colorimetric method was developed.

Procedure.—100 cc. of the brine are made alkaline with Na_2CO_3 and are evaporated to dryness. It is then taken up in water and filtered into a 250-cc. flask. It is made distinctly acid with H_2SO_4 and is diluted to the mark: 25 cc. are pipetted into a 50 cc. Nessler tube and chlorine is added until the maximum colour has developed: 10 cc. of carbon tetrachloride are then added, and the mixture is shaken and compared with a set of standards made up from NaBr solution in the same way. By this rough check the approximate amount of bromine will be discovered, and a set of standard solutions are then prepared which are very close above and below the unknown solution. Again 25 cc. are taken, chlorine water is added to a maximum colour, and the same amount is added to the standards; the sample is then shaken with 10 cc. of CCl_4 and poured into a wet filter; when the water has drained off the filter should be punctured and the liquid caught in a 25-cc. Nessler tube (this is best done in a darkened room, but darkness is not essential). If a sample does not exactly match the standard the colours can be compared by diluting with CCl_4; or since the operation is so simple, a new set of standards can be made up, and then a new determination made. If a test shows that all bromine was not extracted by 10 cc. of CCl_4 a second extraction should be made. This is generally not necessary.

Traces of iodine which are present in most brines will not interfere. The iodine need not be reported.

It is difficult to appreciate the unreliability of published statements regarding the occurrence of bromine. For instance, although the State of Michigan report, and the most reliable information states, that Midland, Mich., brine contains 0·1 per cent of bromine, yet the most exhaustive German work on bromine—("Monographie u. Angewandte Electrochemie, über d. Elektrolytische Gewinnung von Brom," by Max Schlötter)—states on page 3 that the brine from Midland, Ohio, *sic.*, contains 4·18 per cent magnesium bromide, which is equivalent to 3·63 per cent bromine, or 36 times stronger than those who operate on it claim it to be.

Reporting Results.

The results should be reported in such a manner as to give the manufacturer the thing which he wants. The reporting of the constituents as ions, while strictly scientific, is of no value to the manufacturer. All of the sodium and potassium should be calculated to chloride. Since the $CaSO_4$ separates on the copper tubes in the evaporators the H_2SO_4 should be reported as calcium sulphate. The bromine should be calculated as magnesium bromide, since it has long been so considered in the trade; but bromine as free bromine should also be reported. The residual calcium and all the magnesium are calculated to chlorides since they go on the market as such. Strontium and barium should be given as chlorides. The silicon should be reported as the oxide since the form in which it is combined is not known. Iron and aluminium are reported together as oxides since their separation is too time-consuming. The residue which separates on standing should also be given. Results are preferably reported in percentages, though some manufacturers are accustomed to *grms. per litre*. The specific gravity and temperature should always be reported; for this reason also a standard temperature should be used, so that results would be really comparable.

When the positive and negative ions are calculated to compounds they should nearly satisfy each other. It should be borne in mind, however, that the iron, aluminium, and silicon are given as oxides, and not as salts, in which form they usually occur in the brine. There may also be small amounts of CO_2 and iodine which are not included. If, however, the check is not reasonably close it indicates an error, or else some undetermined constituent is present.

	Eastern Ohio, coal mine.	Southern Ohio, driven well.
Specific gravity	1·034	1·180
Baumé equivalent	4·8°	22·2°
Sodium chloride (per cent)	3·26	12·08
Magnesium bromide	0·007	0·124
Bromine	0·006	0·107
Calcium chloride	1·63	10·81
Magnesium chloride	0·05	2·61
Calcium sulphate	0·001	0·03
Iron and aluminium oxides	0·21	0·04
Silica	0·12	0·002
Residue on evaporation	5·23	29·00

As an illustration of the extremes in composition which the analyst must expect to meet, two examples from Ohio brines are given above.

While this work considers primarily the commercial natural brines, the same procedure will doubtless apply to the analysis of artificial brines, such as used in soda-ash manufacture and in electrolytic cells, although the amounts of calcium and magnesium will be much less in these solutions.—*Journal of Industrial and Engineering Chemistry*, ix., No. 7.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, October 17, 1917.

Mr. W. F. J. Wood, B.Sc., President, in the Chair.

The following paper was read:—

"*The Use of Semi-automatic Glass Making Machinery in America.*" By Robert E. McCauley, of Swissvale, Pennsylvania, U.S.A.

The author opened his paper with a discussion of the difficulties met with in the introduction of machinery in America and stated how these difficulties were overcome, particular emphasis being laid on the fact that wages in many cases were doubled by the introduction of automatic machines into the glass industry. He next discussed, from the historical point of view, various types of machines and presses, showing how the most modern up-to-date machine developed. Different types of press and blow machines and machines for making narrow mouth bottles were described in detail, and many interesting facts as to their mode of working were brought out. Points of difference between British and American machines were made clear, and the advantages of the latter from the standpoint of production in bulk being emphasised.

The paper concluded with a description of the use and abuse of machinery in glass houses.

A long and interesting discussion ensued, Messrs. Connolly, Foster, Pitt, Simpson, Hood, Crowther, and Swann all taking part, whilst Mr. McCauley replied at length.

NOTICES OF BOOKS

Our Analytical Chemistry and its Future. By William Francis Hillebrand, Ph.D. New York: Columbia University Press. 1917. Pp. 36. Price 1s. 6d. net.

In this lecture emphasis was laid upon the recent comparative neglect of analytical chemistry, and special attention was called to the need for more research work upon refined methods of examining many substances of the greatest commercial importance. The lecturer alluded to some deficiencies in the education of students of analytical chemistry, and pointed out how some of the defects might be remedied by increasing the number of teachers, lengthening the time given to the subject, and similar measures. He believes that there is need for a permanent institution of analytical chemistry, in which skilled analysts will devote themselves to the study of different methods, and the preparation of standard solutions, in close co-operation with works laboratories. This central institution, the establishment of which he discusses at some length, might finally come to be regarded as a court of appeal and a clearing house of information, its work coming under three heads—Research, Referee, and Education. The need for such an institution is perhaps even greater in this country than in the United States, and those who are interested in the state of scientific work in England will find that the lecture gives them some food for reflection and many new ideas.

Journal and Proceedings of the Royal Society of New South Wales for 1916. Vol. I. Sydney: Published by the Society. London: George Robertson and Co. Pp. 276+lxi.

The *Journal of the Royal Society of New South Wales* contains the Presidential Address for 1916, in which the President, Dr. R. Greig-Smith, reviewed the events of the past year, and discussed the relations of science to industry, a topic upon which every scientific man has nowadays a good deal to say. He also gave some accounts of modern methods of utilising various classes of trade waste, and made suggestions as to some lines of investigation which might profitably be followed up. A considerable part of the Address was devoted to the discussion of recent work on soil fertility, with special reference to the microbiology of the soil. The journal contains papers on biological and other subjects and abstracts of the proceedings of the meetings of the Society.

The Principles and Practice of Sampling Metallic Metallurgical Materials with Special Reference to the Sampling of Copper Bullion. By Edward Keller. Washington: Government Printing Office. Pp. vii.+102. Price 20 cents.

This bulletin contains an exhaustive account of an investigation of the theory and practice of sampling, the theoretical aspects being, in particular, very well treated and the main principles explained in full detail. The author has done a considerable amount of experimental work for the purpose of preparing the report, visiting many works, and obtaining valuable information from various sources, and the bulletin may be regarded as giving the latest and most complete information relating to the sampling of copper bullion which is obtainable. No pains have been spared to arrive at a precise knowledge of the simplest and best methods of sampling, and the final conclusion reached is that both shot sampling and the sampling of the solid materials are equally reliable.

Armstrong College, Newcastle-upon-Tyne. Prospectus of Day Classes. London and Newcastle-upon-Tyne: Andrew Reid and Co., Ltd. 1917.

This prospectus of the classes of the session which has just opened contains the syllabuses of the courses of work provided and the time-tables for the year. The regulations and details of fees, scholarships, examinations, &c., are also included. The buildings of the College have been in the occupation of the War Office since August, 1914, and the departments are temporarily housed in various buildings in Newcastle, lists of which are given in the prospectus.

Report of the Royal Ontario Nickel Commission. Toronto: A. T. Wilgress. 1917. Pp. 584+219.

This large volume gives a detailed account of the work of the Ontario Nickel Commission which was begun in September, 1915. The Commissioners visited important nickel works in all parts of the world, and instituted a thorough investigation of the literature of the subject. All the refineries and smelting plants in Ontario were also visited, and the question of mining taxation was thoroughly threshed out, a large number of witnesses and experts being examined by the Commissioners. The whole mass of evidence collected is contained in this report, which gives very full accounts of the early history of nickel mining in Ontario, the properties and uses of the metal, and alloys and compounds of which it is a constituent. Complete statistics are given of the output of all countries, costs of refining, and exports and imports, and a very exhaustive bibliography is provided. The Commissioners have no hesitation in affirming that nickel can be economically refined in Ontario, and that the province will be able to compete successfully as a nickel producer with any other country. The ore deposits are very extensive and offer excellent facilities for production at a low cost, while any refining process could be worked easily and cheaply in the province. The most satisfactory method of refining would in all probability be the electrolytic, and the establishment of a refining industry would directly benefit the country in many ways.

Operating Details of Gas Producers. By R. H. Fernald. Washington: Government Printing Office. 1916. Pp. 74. Price 10 cents.

This bulletin contains information which hss hitherto been practically unobtainable in a complete form, and the Bureau of Mines has done a useful work in making it available. By sending out a series of questions to owners of producer-gas plants, especially those using bituminous coal and lignites, information was obtained concerning the nature of the fuels and their quantity, the composition and heat value of the gas, methods of operating and cleaning, &c. Many of the answers obtained were somewhat indefinite, and cost data were practically unobtainable, but at the same time the bulletin provides a basis for further discussion and investigation on the part of those interested in the preparation of producer gas.

The Sir John Cass Technical Institute, Jewry Street, Aldgate, E.C. Syllabus of Science Departments, Session 1917-1918.

The Sir John Cass Technical Institute provides courses of instruction for those engaged in chemical, metallurgical, and electrical industries, while the course in experimental science covers the work required for the London University examinations in chemistry, physics, and pure and applied mathematics. Some special courses of higher work have also been arranged in brewing and malting, for example, and the microbiology of the fermentation industries, and in the metallurgical department on gold, silver, and allied metals, iron and steel, metallography and pyrometry, the heat treatment of metals and alloys, and on the mechanical testing of metals and alloys. Special lectures are also given in the physics department on the methods of differential and integral calculus and their application to chemical and physical problems, and in spite of the difficulties caused by the war the Institute is providing instruction of a more general character than hitherto, especially in chemistry, metallurgy, and physics.

CORRESPONDENCE.

ESTIMATION OF FREE SULPHURIC ACID.

To the Editor of the Chemical News.

Sir,—Being a regular reader of your paper I should be glad to know if anyone could suggest a method, or tell me where I could find it, for the estimation of free sulphuric acid in waste water which runs from a works where they pickle steel sheets in sulphuric acid and then wash them in water, which is afterwards allowed to run waste. The water contains a considerable quantity of ferrous sulphate, and perhaps a little sodium sulphate, besides oxide of iron and traces of other impurities. The difficulty I have found in a volumetric analysis is that the precipitation of iron hydroxide on titrating with sodium hydroxide masks the indicator, and I therefore cannot obtain a sharp end-point. If you could enlighten me on this point I should be very much obliged. I should also be glad if you could give me the name of a volume of analyses of waters which you can recommend.—I am, &c.,

H. P. Naucollas,
Head Chemist to Messrs. The Bynea Steel Co., Loughor.

Braeside, Llanelly, October 29, 1917.

MISCELLANEOUS.

Notice of Removal.—The Silica Syndicate, Ltd., announce that they have removed from 82, Hatton Garden, E.C., to 28, Victoria Street, S.W. 1, where all correspondence should be addressed. Telephone—Victoria 5469.

Support for Italy.—Sir R. Vassar Smith, Bart. (who has been elected President of the Federation of British Industries for the forthcoming year, in succession to F. Dudley Docker, C.B.), has sent the following telegram to Signor Orlando, the Premier of Italy:—"The Federation of British Industries extends its full sympathy to the Italian Army and Nation in the present crisis, and pledges its members, whose joint capital represents over two thousand million sterling and who employ some 3,000,000 workpeople, to stand unreservedly behind the British and Allied Governments in furnishing to Italy any support which they may deem necessary."

The "Sanitas" Company, Ltd.—At a Board Meeting of the Company, held on October 26, it was resolved to pay an interim dividend at the rate of 7½ per cent per annum for the six months ended September 30 last.

Estimation of Chromium in Ferrochromium, Steel, and Slags by the Permanganate Method.—P. Koch (*Chem. Zeit.*, 1917, xli., 64; through *Journ. Soc. Chem. Ind.*, 1917, xxxvi., 552).—From 0·2 to 0·3 grm. of the finely divided material is weighed into a porcelain crucible, 4 grms. of sodium peroxide added, and the mixture fused by heating carefully with a small flame, or on a sand-bath, so as to avoid too high a temperature. When cold the product is extracted in a beaker with a litre of boiling water, which is then boiled for a further half-hour to decompose the hydrogen peroxide. The solution is acidified with sulphuric acid to dissolve the ferric oxide, and a measured excess of ferrous sulphate solution is added, when the yellow colour of the chromic acid changes to that of green chromium sulphate, and the excess of ferrous sulphate is titrated with permanganate solution. The end-point, which is indicated by the disappearance of the green colour due to ferrous salt, is best observed by diluting the solution with water to 2 litres. The red colour of the permanganate is masked by the complementary colour of the chromium salt. The titration of all chromium solutions requires to be conducted rapidly. The analysis of chromium alloys by liberation of iodine by chromic acid and titration with thiosulphate gives an erroneously high value for the chromium through the presence of other compounds which liberate iodine. If the fusion with sodium peroxide is made in a nickel crucible the solution must be freed from particles of nickel and nickel oxide by filtration before acidifying. An alternative method, applicable to the estimation of chromium in steels, consists in dissolving 1 grm. of the metal in dilute sulphuric acid, oxidising with saturated potassium permanganate solution until the red colour of the latter persists on continued boiling, adding 10 to 20 cc. of manganese sulphate solution, filtering from the separated manganese dioxide, and then adding standard ferrous sulphate solution and titrating with potassium permanganate. With slags containing manganese, 3 to 5 grms. are well mixed with 20 to 40 grms. of sodium peroxide and heated in a crucible of nickel, iron, or copper until disintegration of the slag is complete, the product is extracted with hot water, boiled, and the residue containing manganese dioxide and the oxides of silicon and iron is filtered off. The small quantity of manganese which is held in solution as manganate and permanganate is decomposed as before by boiling the acidified solution with a few cc. of manganese sulphide, and the solution is filtered and the chromium estimated by adding ferrous sulphate and titrating back with potassium permanganate or N/10 potassium chromate or bichromate.—*The Analyst*, xlii, No. 497.

MEETINGS FOR THE WEEK

Monday, 12th.—Biochemical Society, 5.30. (In the Pathological Department, Guy's Hospital, S.E.). "Bacterial Products and Plant Growth," by W. B. Bottomley. "Influence of Diet upon Tumour Growth," by J. C. Drummond. "Relative Behaviour of Antineuritic and Antiscorbutic Factors towards Adsorbents," A. Harden and S. S. Zilva. "Antiscorbutic Properties of Milk," by E. Margaret Hume and Ruth Skelton.

Thursday, 15th.—Royal Society. "Investigation into the Inhibition exhibited by some Shellac Derivatives," by A. P. Laurie and C. Ranken. "Phenomena connected with Turbulence in the Lower Atmosphere," by G. I. Taylor. "Relation between Barometric Pressure and the Water Level in a Well at Kew Observatory," by E. G. Bilham.

To comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

Analytical and Metallurgical Chemist seeks Re-engagement. Sound experience in all Steel and Alloys Analysis and General Assaying. University trained man. Excellent references. Ineligible.—Address, "Metal," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Assistant Chemists required, to carry out Research Work of national importance. Liberal salary. University trained preferred.—Address, P., I., and R., Ltd., 186, Walmer Road, Notting Hill, W. 11.

Chemist seeks Engagement. Post with scope for organising ability preferred. Fifteen years' Laboratory experience; Organic and Inorganic Research, Foods and Drugs, Steels, Alloys, Plant Products, Tobacco, &c.—Address, "Ova," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Chemist, well up in Oils, Fats, and Organic Chemistry, required for Food Factory in South-West. State age, qualifications, and experience.—Address, "Catrac," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Engineering Chemist required by large fuel consumer, to carry out Research Work on all classes of Fuels and to deal with Water Problems. Commencing salary £156 per annum.—Address, Yorkshire Electric Power Company, Wellington Road, Dewsbury.

Women or Men Analytical Chemists required at salary of £150 per annum in Government Department, South of England.—Address, G. D., Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted, for Oil Refining and Hardening Works, TWO COMPRESSORS—one of 8000 cubic feet per hour and one of 24,000 cubic feet per hour; CONTROL APPARATUS, clock pattern; ELECTRICAL THERMOMETER for Catalyser; TWELVE 3-inch CENTRIFUGAL PUMPS; ONE BLOWER, 60 Centigrade water pressure; TWENTY-TWO TANKS—ten of 20-ton capacity, four of 15-ton capacity, eight of 10-ton capacity, the last to be wooden or lead-faced.—Write, with full particulars, to Box 429, care of Mather and Crowther, Ltd., 10-13, New Bridge Street, London, E.C. 4.

Wanted, "MEMORIALS OF THE GOODWIN SANDS," by Mr. Gattie.—Address, W. S., Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

The Proprietors of PATENT No. 21477 of 1913, for
"PROCESS FOR CONVERTING UNSATURATED FATTY ACIDS AND THEIR ESTERS INTO SATURATED COMPOUNDS."
are desirous of entering into arrangements by way of Licence and otherwise, on reasonable terms, for the purpose of exploiting the same and ensuring its full development and practical working in this country. All communications should be addressed in the first instance to HASELTINE, LAKE, and CO., Chartered Patent Agents, 28, Southampton Buildings, Chancery Lane, London, W.C. 2.

THE CHEMICAL NEWS

VOL. CXVI., No. 3025.

ANALYSIS OF WHITE METAL ALLOYS; DETERMINATION OF LEAD, COPPER, AND ANTIMONY.

By R. HOWDEN, B.Sc Edin.

Lead.—One grm. of the alloy is dissolved in nitrohydrochloric acid. To the solution is added 5 cc. of concentrated sulphuric acid and a grm. or so of tartaric acid. The solution is evaporated on the hot plate till red fumes cease to come off. This happens quite suddenly; the solution rapidly changes colour from yellowish green to pale blue, and becomes tranquil. As soon as this takes place it is removed from the hot plate and diluted. The lead falls as sulphate; it is collected on the filter, washed, burnt off, and weighed.

Copper.—Sulphur dioxide is passed into the filtrate from the lead sulphate, and the copper is precipitated as cuprous iodide or as thiocyanate. The precipitate is collected on a pulp filter, dissolved in diluted nitric acid, and the copper estimated by the iodide and thiosulphate method.

Antimony.—One grm. of alloy is dissolved in hydrochloric acid with the aid of potassium chlorate. To the solution is added, drop by drop, a solution of stannous chloride till the yellow colour due to the copper is bleached. The solution is then diluted to a convenient bulk, and air is aspirated through it for about twenty minutes to reoxidise the copper.

The solution being thus prepared the antimony is estimated by the bromate method. This method consists in reoxidising the antimony by a standard solution of potassium bromate. A convenient strength is 4·639 grms. to the litre, 1 cc. being equivalent to 1 per cent of solution when 1 grm. is taken. The solution to be titrated is coloured with a drop of an organic colouring matter such as methyl-orange. The bromate solution is run in until one drop suddenly destroys the colour of the methyl-orange. The titration is performed at a temperature of about 60° F.

NEW DERIVATIVES OF TUNGSTEN.

By J. BENNETT HILL.

As early as 1859, Blomstrand (*Journ. Prakt. Chem.*, 1859, lxxvii., 88) reported a series of compounds of molybdenum derived from the dihalides $MoCl_2$ and $MoBr_2$. These dihalides had been obtained by repeated volatilisation of the trihalides in a current of carbon dioxide. The non-volatile product was soluble in alkalis, and from this solution hydrates of the type $Mo_3Cl_4(OH)_2$ were precipitated by weak acids. All of these derivatives were yellow in colour. They could be dissolved in strong acids, the nitric acid solutions showing no ionised halogen. The hydrochloric acid solution of the chloromolybdenum hydroxide gave on crystallisation $Mo_3Cl_6.6H_2O$, and on dilution a pale yellow insoluble compound, $Mo_3Cl_6.3H_2O$. Mixed halogen derivatives, such as $Mo_3Cl_4Br_2\ 6H_2O$ and $Mo_3Br_4Cl_2.6H_2O$ were also obtained. The chemistry and constitution of these compounds was further developed by Atterberg (*Jahresb.*, 1872, 260), and Liechti and Kempe (*Ann.*, 1873, clxix., 354). Muthmann and Nagel (*Ber.*, 1898, xxxi., 2009), Rosenheim and Kohn (*Z. Anorg. Chem.*, 1910, lxvi., 1), and Koppel (*Z. Anorg. Chem.*, 1912, lxxvii, 289). Muthmann and Nagel determined the molecular weight of molybdenum dichloride dissolved in ethyl alcohol, and found it to correspond to the triple formula Mo_3Cl_6. Rosenheim and Kohn prepared a compound, $Mo_3Cl_6.HCl.4H_2O$, by dissolving Mo_3Cl_6 in strong hydrochloric acid, evaporating on a water bath and allowing the solution to crystallise. The compound consisted of glistening yellow needles, soluble in hydrochloric acid, but was hydrolysed by pure water. Only three-sevenths of the chlorine in the compound were ionised.

In 1909 Chapin (*Journ. Am. Chem. Soc.*, 1910, xxxii., 323) described halide bases of tantalum. He prepared these compounds by a method previously used by Chabrie (*Comptes Rendus*, 1907, cxliv., 804) for obtaining what he called the dichloride of tantalum. It consisted in heating the pentachloride with 3 per cent sodium amalgam in a hard glass tube sealed at one end and evacuated by means of a suction pump. Chapin used the pentabromide of tantalum. The reaction mass, taken up with water and hydrobromic acid and evaporated, furnished a crystalline body, $Ta_6Br_{14}.7H_2O$, dissolving in water to a dark emerald green solution. Chapin further showed that only one-seventh of the bromine in this compound was ionised, indicating the formula $(Ta_6Br_{12})Br_2.7H_2O$. As additional evidence of the correctness of this formula he prepared a number of derivatives of the radical Ta_6Br_{12}. *e.g.*, $(Ta_6Br_{12})Cl_2.7H_2O$, $Ta_6Br_{12}(OH)_2.10H_2O$, and others. He determined the molecular weight of the parent bromide in propyl alcohol and found it to correspond to the formula given.

In 1913 Harned (*Journ. Am. Chem. Soc.*, 1913, xxxv., 1078) reported a similar series of compounds of columbium obtained from the pentachloride by the Chabrie method. He obtained a crystalline body, $(Cb_6Cl_{12})Cl_2.7H_2O$, soluble in water to an olive green solution, a crystalline hydroxide, $Cb_6Cl_{12}(OH)_2.8H_2O$, and others. Both the columbium and tantalum compounds were characterised by their remarkable tinctorial power, a milligrm. being sufficient to colour 100 cc. of water an intense green.

Harned also obtained a brown compound, insoluble in water, the analysis of which corresponded to the formula $Cb_6Cl_{14}\ 9H_2O$. This was prepared by the addition of concentrated hydrochloric acid to the alkaline solution of the green compound $(Cb_6Cl_{12})Cl_2.7H_2O$. The brown derivative, on boiling with water, slowly reverted to the original green. His experiments led him to the conclusion that there was a constitutional difference between the two.

In view of the existence of these compounds of molybdenum, tantalum, and columbium, it would seem reasonable to expect that the closely related element, tungsten, would form similar derivatives. Roscoe (*Ann.*, 1872, clxii., 360) reported the dichloride, dibromide, and diiodide, but a more thorough investigation of them has never been carried out. The present work was undertaken to prepare, if possible, bodies of tungsten similar to those of molybdenum, tantalum, and columbium.

To get pure tungsten trioxide from wolframite, the method of purification was that employed by Smith and Exner (CHEM. NEWS, 1904, xc., 37). The reduction of the pure oxide of tungsten by hydrogen was carried out in a quartz tube, heated to a little over 1000° in a gas-heated furnace constructed of asbestos. The resulting metal with a pale grey colour was changed to hexachloride by the process of Smith and Exner, and need not be mentioned here. It was found, however, that, while commercial tungsten could be converted to hexachloride at the rate of about 20 grms. in two hours, the pure material as obtained above was only very slowly attacked, seven hours being required to effect the chlorination of 10 grms. of metal. Since there was only a trace of oxychlorides formed in the reaction, it was thought that possibly their presence might exert a catalytic action on the chlorination. In an attempt to catalyse the reaction in another way, 0·1 grm. of precipitated platinum was sprinkled on the tungsten in the boat. On passing chlorine over the gently heated boat no difference in the speed of the reaction was at first noticed. After a few minutes a glow appeared to run through the mass, and from this point on the reaction took place as fast as the chlorine could be passed in, the chlorine uniting with the metal with incandescence. By this means 20 grms. of tungsten were converted to hexachloride in 1½ to 1¾ hours. After the tungsten had been swept out, the platinum remained on the bottom of the boat as a brown powder. This was used in the chlorination of the next batch of tungsten and so on repeatedly. Three hundred grms. of pure tungsten hexachloride were so obtained.

To reduce the hexachloride in the method outlined by Chabrie and by Chapin, it was mixed in a mortar with a little less than the amount of powdered 3 per cent sodium amalgam calculated to reduce it to the state of dichloride. The mixture was quickly transferred to a Jena tube sealed at one end. The tube, after connecting with a suction pump and evacuating, was gently heated until the reaction had taken place, and then heated strongly for about ten minutes. It was allowed to cool in the vacuum, and the contents extracted with hydrochloric acid. On filtering there was obtained a deep reddish brown filtrate and a grey precipitate. Attempts to crystallise the highly coloured compound from this solution failed. Its solution was very stable in the air and could be evaporated to dryness with only a trace of decomposition.

Before preparing any quantity of the brown solution the conditions of the reaction were investigated, varying the proportions of the reacting substances and the temperature and duration of heating. As a result the following details were adopted:—15 grms. of tungsten hexachloride were ground in a mortar and mixed carefully and quickly with 105 grms. of sodium amalgam. The reaction between the two substances is rather vigorous, and, unless precautions are taken to prevent it, is liable to take place in the mortar. In view of this the mortar, as well as both of the reacting substances, were cooled in ice previous to the mixing. In addition to this, not more than ten seconds were allowed to elapse between the time when the amalgam was brought in contact with the hexachloride and the time when the mixture was in the Jena tube with the vacuum on. In spite of these precautions the reaction frequently took place during mixing. When the mixing and transfer to the tube had been successfully accomplished the reaction was allowed to take place, and the tube then heated just to dull redness and allowed to cool immediately. The contents were extracted with hydrochloric acid (sp. gr. 1·08), and the solution filtered. The brown colour so obtained was intense.

A portion of the brown solution was evaporated to dryness and the dry residue extracted with alcohol. A dark reddish brown solution resulted, from which nothing could be crystallised. An extraction with ether gave a yellow solution, which on evaporation left a pale yellow amorphous body. This, taken up with a drop of dilute hydrochloric acid and allowed to evaporate, showed under the microscope shining yellow needles. A somewhat larger portion of the dry residue, treated in a similar way, gave needles as much as a centimetre in length. Experiments with the original brown solution of the reduced mass led to the following method of isolation of the yellow needles. The brown solution was boiled down until considerable sodium chloride had separated out, when it was filtered hot and allowed to cool. There then separated a mixture of sodium chloride and the yellow needles. This was filtered off and washed with concentrated hydrochloric acid until the liquid came through almost colourless. The mixture was spread out on a watch-glass and allowed to dry in the air. It was next extracted for about ten minutes under a reflux condenser with ether containing about 5 per cent of ethyl alcohol. The insoluble sodium chloride was filtered out and the ether distilled off from the filtrate, leaving a yellow amorphous mass. This was taken up with fairly strong hydrochloric acid, and boiled, when everything dissolved. The clear yellow-coloured solution was evaporated to small bulk and allowed to cool, when an abundance of yellow needles separated. These were filtered off, washed with concentrated hydrochloric acid, and dried in the air. From 150 grms. of tungten hexachloride 12 grms. of the yellow compound were obtained.

It proved to be readily soluble in alcohol, acetone, glacial acetic acid, and in ether containing alcohol, but was almost insoluble in pure anhydrous ether. It was insoluble in benzene, carbon bisulphide, carbon tetrachloride, and chloroform. It dissolved in water, but the aqueous solution on standing hydrolysed, precipitating out first a yellow and then a black compound. The crystals on long exposure to air, or in a desiccator over sulphuric acid, disintegrated, giving a lemon-yellow amorphous compound, insoluble in water. The same compound was produced on allowing the solution in dilute hydrochloric acid to stand or on diluting it with water. The resemblance of these two compounds to Rosenheim and Kohn's $Mo_3Cl_6.HCl.4H_2O$ and Blomstrand's $Mo_3Cl_6.3H_2O$ will be at once noticed.

Warm nitric acid effected a complete decomposition of the solution of the yellow needles, a hydrated tungsten trioxide being precipitated in granular form. Potassium hydroxide added to an aqueous solution of the compound gave a clear yellow-coloured solution which darkened immediately to a deep brown. From this solution weak acids threw down a black gelatinous precipitate. The same compound was obtained by treating the aqueous solution of the yellow needles with sodium carbonate. The brown alkaline solution on exposure to the air slowly faded in colour to a deep yellow, which with weak acids yielded a yellow gelatinous precipitate.

The determination of tungsten in the yellow needles was obtained by a very simple and direct method. The compound was weighed out in a porcelain crucible, covered with concentrated nitric acid, and digested for several hours on a water bath. It was then evaporated to dryness, ignited, and weighed as WO_3. Result 1 and 2 were obtained by this method; the analyses were made with different preparations of the compound, the result giving evidence both of the accuracy of the method of analysis and of the homogeneity of the product. The third determination was obtained by an altogether different procedure. The aqueous solution of the compound was treated with potassium hydroxide and the deep brown solution acidulated with acetic acid. The black precipitate was filtered off and ignited to trioxide.

No.	Wt. sample.	WO_2 found	W p. c.
1.	0·2223	0·1752	62·50
2.	0·2271	0·1787	62·42
3.	0·2009	0·1586	62·62
			Average, 62·51

The determination of chlorine offered much greater difficulty. It would be fruitless to enumerate the methods attempted. Most of them were valueless for the reason that the silver chloride was contaminated with tungsten. It might be mentioned here that the presence of as little as ½ per cent of tungsten in this precipitate completely alters its character, the silver chloride separating in a granular form rather than curdy. Of the methods attempted the following appeared to be the most satisfactory:—

Method 1.—The compound was dissolved in water, treated with ammonia, and the solution oxidised with ammonium persulphate. The excess ammonia was boiled off, the tungsten precipitated out as cadmium tungstate, and the chlorine determined in the filtrate as silver chloride. Determination 1 was obtained by this method.

Method 2.—The solution of the compound was treated with sodium carbonate and boiled. The black precipitate was filtered out and the silver chloride precipitated in the filtrate. The precipitate showed considerable contamination with tungsten, and was dissolved in ammonia and reprecipitated. Determinations 2 and 3 were obtained in this way.

Method 3.—The compound was dissolved in nitric acid (sp. gr. 1·1) and warmed for about two hours, when the tungsten completely separated as the hydrated trioxide. This was filtered off, and the chlorine determined as silver chloride in the filtrate. The precipitate showed no contamination with tungsten. The results are determinations 4 and 5.

No.	Wt. sample.	AgCl found.	Cl p. c.
1.	0·2039	0·2351	28·53
2.	0·1999	0·2298	28·43
3.	0·2014	0·2329	28·62
4.	0·2022	0·2285	27·97
5.	0·2015	0·2269	27·85
		Average,	28·28

The water was estimated by the method used by Chapin. The material was mixed with dry lead oxide, and heated in a boat in a current of pure dry air to about 300° for two hours. The water was collected in a weighed calcium chloride tube. The details of manipulation are those outlined by Chapin.

No.	Wt. sample..	H_2O found.	H_2O p. c.
1.	0·2007	0·0203	10·11
2.	0·2008	0·0206	10·26
		Mean,	10·18

It should be noted that the hydrogen of any hydrochloric acid in the molecule of the compound would appear here as water along with the true water of the compound. The theoretical compositions calculated below are figured on this basis, and will therefore add up to more than 100 per cent.

It was expected that the composition of the compound would correspond to the formula $W_3Cl_6 \cdot HCl.4H_2O$, analogous to Rosenheim and Kohn's $Mo_3Cl_6 \cdot HCl.4H_2O$. It will be seen on reference to the figures that the observed values do not agree with those calculated for this substance. They agree much better with the calculated percentages for a compound containing another half molecule of water, the doubled formula of which would be $W_6Cl_{12}.2HCl.9H_2O$. The calculated compositions follow:—

Per cent.	Calculated for $W_3Cl_6HCl.4H_2O$.	Calculated for $W_6Cl_{12}.2HCl.9H_2O$.	Observed.
W	63·20	62·55	62·51
Cl	28·46	28·16	28·28
H_2O ..	9·27	10·20	10·18

The doubled formula finds support in its analogy with the tantalum and columbium compounds. It finds a complete analogy in the columbium compound prepared by Harned and formulated by him, $Cb_6Cl_{14} \cdot 9H_2O$.

Since the compounds of molybdenum, tantalum, and columbium ionise only part of their chlorine in aqueous solution, it seemed reasonable to expect that the yellow tungsten compound would behave similarly. Accordingly an attempt was made to determine the amount of chlorine ionised. In view of the fact that the compound is hydrolysed in pure water or in dilute acids other than hydrochloric, the problem presented considerable difficulty. The first attempt was to dissolve it in potassium hydroxide solution and to add to the deep brown solution acetic acid, throwing out the black gelatinous precipitate. This was filtered off and the chlorine determined in the filtrate. The operation was conducted entirely in the cold. A similar treatment of the molybdenum compound precipitated a hydrated $Mo_3Cl_4(OH)_2$, leaving the ionised chlorine in the filtrate. The same behaviour was expected here. The following results were obtained:—

Wt. sample = 0·2009 AgCl found = 0·2291
Cl = 28·21 per cent

This corresponds to the total chlorine in the compound, indicating that a complete decomposition had taken place and that the black precipitate contained no chlorine.

A second attempt was based on the fact, previously mentioned, that the brown alkaline solution on standing fades to a brownish yellow, and that from this solution acetic acid precipitates a yellow-coloured substance. A sample of the yellow needles was dissolved in alkali and so treated, the chlorine being determined in the filtrate.

Wt. sample = 0·1017 AgCl found = 0·1182
Cl = 28·76 per cent

The result again indicated a complete decomposition of the needles. It would seem probable that if derivatives in which only a part of the chlorine is split off are formed at all, they are extremely unstable.

In order to provide further evidence in favour of the formula assigned to the yellow compound, a determination of the molecular weight was sought. An attempt was first made to arrive at this by the lowering of the freezing point of glacial acetic acid. It was discovered, however, that the water of crystallisation of the compound interfered to such an extent that no result could be obtained by this method. The rise of the boiling point of ethyl alcohol was next attempted. Here the hydrochloric acid in the molecule appeared to interfere, the boiling point falling on solution of the compound rather than rising. A further investigation along these lines was prevented by lack of material.

Other Related Compounds.

The lemon-yellow-coloured amorphous compound has been described. About a grm. of this material was prepared from the yellow needles. It was soluble in boiling hydrochloric acid, reverting to the original yellow derivative. It dissolved in alkalis to give the deep brown solution. Analysis gave the following results:—

Wt. sample =				Per cent.
0·2003	WO_3 found =	0·1716	W =	67·95
0·2074	AgCl found =	0·2325	Cl =	27·73
0·2007		0·2236		27·57
0·1063		0·1169		27·20
0·2001	H_2O found =	0·0107	H_2O =	5·35

These values do not correspond to any reasonable formula, and it is probable that the compound prepared was impure.

An investigation of the mother liquors from the crystallisation of the yellow needles led to the isolation of another compound crystallising in dark brown shining needles. This was prepared by slowly saturating the mother liquor with hydrochloric acid gas and letting it stand for several days. The sodium chloride thrown out contained, besides yellow needles, a small quantity of the brown compound in crystals about 2 mm. long. The mixture was dried and the brown needles picked out. Only a few milligrms. were obtained. They dissolved in water to a clear yellow-coloured solution, not decomposed by boiling nitric acid nor by potassium hydroxide. Sodium carbonate threw out a yellow granular precipitate. The tinctorial power of the compound was remarkable, one of the small crystals giving a decided colour to 100 cc. of water. This fact makes it probable that the substance is related to the tantalum and columbium compounds. No analysis was obtained owing to the small amount of substance at hand.

Investigation of the Alkaline Solution of the Yellow Needles.

It has been mentioned that the addition of alkali to an aqueous solution of the yellow needles produced three distinct solutions—first, a yellow-coloured solution, which changed immediately to a deep brown, which in turn changed slowly on exposure to the air to a less highly coloured brownish yellow solution. It was undertaken here to determine the state of oxidation of the tungsten in these three solutions. The deep brown solution was first investigated. To this end a sample of the yellow compound was dissolved in water and treated with a solution of potassium hydroxide. This solution was let stand for about thirty seconds when it had assumed the dark colour. An excess of standard iodine was then added, the colour fading to a pale yellow. After standing thirty minutes, the solution was made acid with acetic acid and the excess iodine titrated with thiosulphate. The result is No. 1 in the table. It shows that the tungsten is almost completely in the trivalent condition. The determination was repeated, allowing the alkaline solution to stand ten minutes before the addition of the iodine. The result (2 in the table) shows that the tungsten has been completely oxidised to the trivalent state. Since, from the deep brown solution, weak acids threw out the black gelatinous precipitate, which redissolved in alkali to give the original solution, the above results would indicate this black compound to be a hydrated W_2O_3, possibly $W(OH)_3$.

The same method was applied to the brownish yellow solution obtained by letting the alkaline solution stand exposed to the air for twenty-four hours. The result (3 in the table) shows that the solution contains quadrivalent tungsten, and that the yellow hydrate obtained from it by the action of weak acids must be a hydrated WO_2.

The first yellow alkaline solution contains tungsten of undoubtedly the same state of oxidation as the yellow needles. The rapidity with which it oxidises made it rather more difficult to investigate than the other two. To avoid this difficulty the iodine solution was added to the potassium hydroxide, and the mixture then added to the water solution of the yellow compound. It was let stand thirty minutes, made acid, and titrated as before. The result is No. 4. It indicates bivalent tungsten, which was, of course, to be expected.

No.	Wt. sample.	I absorbed.	Calculated for W''.	Calculated for W'''.	Calculated for W''''.
1.	0·1007	0·138	0·174	0·131	—
2.	0·1008	0·131	0·174	0·131	—
3.	0·1016	0·089	—	0·132	0·088
4.	0·1009	0·167	0·174	0·131	—

Summary.

1. The action of chlorine on tungsten metal to form hexachloride is catalysed to a remarkable degree by the presence of a small amount of platinum black.

2. Tungsten forms the compound $W_6Cl_{12}.2HCl.9H_2O$, resembling the molybdenum derivative Mo_3Cl_6 $HCl.4H_2O$, prepared by Rosenheim and Kohn.

3. The alkaline solution of the preceding compound oxidises readily, and from the solution stable hydrates of trivalent and quadrivalent tungsten were obtained.—*Journal of the American Chemical Society*, xxxviii., No. 11.

ON THE QUALITATIVE SEPARATION AND DETECTION OF GALLIUM.

By PHILIP E. BROWNING and LYMAN E. PORTER.

GALLIUM, discovered in 1875 by Lecoq de Boisbaudran (*Comptes Rendus*, lxxxi., 493), is found in nature most closely associated with the elements aluminium, iron, manganese, zinc, lead, and indium (Boulanger and Bardet, *Comptes Rendus*, clvii, 718; Hartley and Ramage, *Journ. Chem. Soc.*, 1897, 533, 547; Hillebrand and Schnerrer, *Ind. Eng. Chem.*, viii., 225).

Analytically it falls into the aluminium group. It may be separated from the bases giving sulphides in acid solution by hydrogen sulphide; from nickel, cobalt, zinc, manganese, the alkali earths, and the alkalis by ammonium hydroxide in the presence of ammonium chloride; and from iron, titanium, thallic thallium, uranium, indium, and the rare earths by sodium hydroxide in excess, in which reagent the hydroxide of gallium is soluble. In the ordinary course of analysis it appears in the group containing aluminium, beryllium, chromium, and vanadium. From the last mentioned two elements it may be separated by ammonium hydroxide after their oxidation to the acidic condition.

This narrows the problem of separation down to the separation from aluminium and beryllium; and the practical absence of beryllium from products containing gallium leaves the most important separation—that from aluminium.

Lecoq de Boisbaudran, in a series of articles published soon after the announcement of his discovery (*Comptes Rendus*, xciv., 1154, 1228, 1439, 1628; xcv., 157, 410, 503, 1192, 1332; xcvi., 152, 1696, 1838; xcvii., 142, 295, 522, 623, 730, 1463), suggested many methods of separation from the other elements, and recommended especially for the separation from aluminium the use of a precipitant of potassium ferrocyanide in the presence of strong hydrochloric acid to about one-third of the volume of the solution (*Comptes Rendus*, xcix., 526).

In previous papers one of us has shown that silver, lead, zinc, copper, and indium have been successfully separated from gallium by various applications and modifications of known methods (Browning and Uhler, *Am. Journ. Sci.*, xli., April, 1916; xlii., Nov., 1916). The object of this paper is to give the results of some work upon the application of potassium ferrocyanide to the separation of gallium from aluminium and beryllium, and to describe the outcome of experiments upon the delicacy of the test for gallium by the ferrocyanide method, upon the decomposition of the ferrocyanide when formed and upon the application of strong hydrochloric acid to the separation of gallium and aluminium.

It was found that when solutions containing about 0·1 grm. of aluminium or beryllium were strongly acidified with hydrochloric acid and treated with potassium ferrocyanide no precipitation took place, while 0·001 grm. of gallium in the presence of 0·1 grm. of aluminium was easily precipitated and detected at once. Amounts of gallium as small as 0·0001 grm. could be detected after the solution had been allowed to stand an hour or so. These tests were generally made in a volume of liquid from about 5 to 10 cc., of which from one-quarter to one-third was strong hydrochloric acid.

With traces of zinc present, the use of potassium ferrocyanide as the precipitant may lead to erroneous conclusions, because zinc ferrocyanide is almost as readily precipitated as the gallium. The presence of zinc may be avoided by the careful application of the ammonium chloride and ammonium hydroxide process. Should, however, traces of zinc remain, we have found that they may be satisfactorily detected and removed by treating a sodium hydroxide solution with hydrogen sulphide, which removes the zinc without precipitating the gallium. The filtrate, which must still be alkaline, is acidified, and free hydrogen sulphide removed by boiling. The sulphur is oxidised by hydrogen dioxide in sodium hydroxide solution, and the boiling is continued to remove the excess of hydrogen dioxide. This solution is then acidified with hydrochloric acid and the usual ferrocyanide test may be made for gallium. Solutions were prepared containing gallium and zinc and were analysed by the experimenter without knowledge of the content. The results are given in Table I.

TABLE I.

	Issued.	Found.
1.	0·001 grm. Ga	Zn absent, Ga present.
2.	0·001 grm. Zn + 0·001 grm. Ga	Zn present, Ga present.
3.	0·001 grm. Zn	Zn present, Ga absent.
4.	Distilled water	Zn absent, Ga absent.
5.	0·002 grm. Zn	Zn present, Ga absent.
6.	0·050 grm. Zn	Zn present, Ga very faint indication.
7.	0·050 grm. Zn + 0·001 grm. Ga	Zn present, Ga present.
8.	0·050 grm. Zn + 0·0002 grm. Ga	Zn present, Ga present.

The faint indication of the presence of Ga in Experiment 6 seemed to indicate a trace of that element in the zinc. It is of interest to note that this indication was not obtained until the solution had stood twenty minutes, while in Experiment 8 the test for the gallium was unmistakeable and practically immediate.

A number of reactions were investigated leading to the decomposition of the gallium ferrocyanide and the recovery of the gallium as the hydroxide, such as treatment with bromine and with nitric acid, and fusion with sodium peroxide and with ammonium nitrate. The most satisfactory proved to be fusion with ammonium nitrate, which destroyed the ferrocyanide radical, and subsequent treatment with sodium hydroxide, which precipitated the ferric hydroxide and left the gallium in solution, from which the hydroxide could be readily precipitated by adding ammonium chloride in excess and boiling.

Gooch and Havens (*Am. Journ. Sci.*, 1896, ii., 416) have shown that iron may be separated from aluminium by saturating solutions containing these elements with hydrochloric acid gas, adding ether, and again saturating. The chloride of aluminium is completely precipitated by this method and the iron remains in solution. This process was applied successfully to the separation of aluminium from gallium. The presence or absence of gallium may be determined by evaporating the filtrate to dryness on a steam-bath and dissolving the residue in dilute hydrochloric acid. This solution, which is free from aluminium, may be tested for gallium by means of potassium ferrocyanide. The series of unknown solutions given in Table II. was tested by this method, the aluminium chloride used having been purified by the hydrochloric acid precipitation.

TABLE II.

	Issued.	Found.
1.	0·0005 grm. Ga	Al absent, Ga present.
2.	0·1 grm. Al	Al present, Ga absent.
3.	0·1 grm. Al + 0·0005 grm. Ga	Al present. Ga present.
4.	Distilled water	Al absent, Ga absent.
5.	0·02 grm. Al + 0·001 grm. Ga	Al present, Ga present.
6,	0·0001 grm. Ga	Al absent, Ga present.

During the first trial of this method, aluminium nitrate was used in hydrochloric acid solution, and it was found that no precipitation took place with potassium ferrocyanide. After treatment with the hydrogen chloride gas and evaporation, however, an indication of gallium was found. This led to an investigation which showed that there was some gallium present in the aluminium nitrate, but that the nitric acid formed by dissolving it in hydrochloric acid was sufficient to prevent the precipitation of the gallium as the ferrocyanide. In the evaporation process the nitric acid is destroyed and the test becomes very delicate.

An investigation was then made of the effect of nitrates in general on ferrocyanides. It was found that when one drop of potassium ferrocyanide is treated with 0·4 grm. of ammonium nitrate in the presence of 6 cc. of 1 : 2 hydrochloric acid, it is oxidised completely to the ferricyanide within two minutes, as may be shown by the use of a ferric salt and a ferrous salt. If 0·2 grm. of ammonium nitrate is used under the same conditions, the ferrocyanide is broken up in less than an hour, while if only 0·1 grm. of ammonium nitrate is used a longer time is required, but complete oxidation finally takes place. Other experiments showed that 0·0001 grm. of gallium cannot be precipitated as the ferrocyanide in 5 cc. of dilute hydrochloric acid in the presence of three drops of dilute nitric acid, whereas it is readily precipitated in the absence of it. If was further found that if 0·0001 grm. of gallium is precipitated and 1 cc. of dilute nitric acid is added, the precipitate is decomposed and dissolved within forty-five minutes. It is thus seen that in detecting gallium by the ferrocyanide method care must be taken to have no nitrates or nitric acid present, and that these may be successfully removed by evaporation with hydrochloric acid.—*American Journal of Science*, xliv., 221.

CHEMICAL NOTES.[*]

A NEW ABSORBENT FOR CO_2 IN STEEL ANALYSIS.

A NEW absorbent for carbon dioxide, termed "soda asbestos," is prepared by mixing a solution of 500 grms. of sodium hydroxide in 500 cc. of water with 1 kilo. of pulverised sodium hydroxide and adding shredded asbestos gradually, with stirring, until the mixture appears not to be capable of wetting more asbestos. The mass is heated at 150—180° C. for four hours, with addition of more asbestos from time to time, then cooled and ground till most of it passes a 10-mesh sieve. A quantity of this absorbent sufficient to fill the tube described above, will absorb 8—10 grms. of carbon dioxide.—G. L. KELLEY, *Journ. Ind. Eng.*, 1916, viii., 1038; *Journal of the Society of Chemical Industry*, Dec. 15, 1916, p. 1237.

LEAD MOLYBDATE.

Lead molybdate, precipitated from ammonium molybdate solution by the addition of lead nitrate solution, is more granular and much less bulky than when lead acetate solution is used as the precipitant; the precipitate obtained with lead acetate may, however, be rendered granular by adding a small amount of nitric acid to the ammonium molybdate solution. Freshly precipitated molybdate is fairly soluble in nitric acid, and slightly soluble in ammonium acetate and sodium acetate solutions, but the solvent action of the small amount of nitric acid used to obtain the precipitate in a condition suitable for filtration may be counteracted by subsequent neutralisation. In the presence of an excess of ammonium molybdate, lead molybdate forms a colloidal solution; the addition of nitric acid reprecipitates the lead molybdate. To determine molybdenum in a soluble molybdate, a quantity of the salt corresponding to about 0·4 grm. MoO_3 is dissolved in 180 cc. of water, a few drops of nitric acid are added, and, to the boiling solution, 4 per cent lead nitrate solution is added, drop by drop, until the addition of a further drop causes the milky mixture to become visibly clearer. The boiling is continued for another three minutes, another drop or more of lead nitrate solution is added, followed by ammonia until the mixture is neutral to litmus paper. The precipitate is collected, washed with 2 per cent ammonium nitrate solution, dried above 100° C., and ignited at a dull red heat, and weighed. $PbMoO_4 \times 0{\cdot}2616 = Mo$. This method may be used, conversely, for the determination of lead.—H. B. WEISSER, *Journ. Phys., Chem.*, 1916, xx., 640; *Journal of the Society of Chemical Industry*, Dec. 15, 1916, p. 1237.

VOLUMETRIC DETERMINATION OF MERCURY.

The method is based on the reduction of mercury salts to metallic mercury by means of formaldehyde in presence of potassium hydroxide. The mercury is treated with excess of a standard iodine solution, the excess of the latter over the amount required to convert the mercury into mercuric iodide being determined by titration with standard sodium thiosulphate solution. The method is rapid and gives very exact results, and is carried out as follows:—One grm. of the mercuric salt or of the mercuric chloride compress is treated with a little water, and, if necessary, sodium chloride to dissolve the mercuric salt, the solution being made up to 250 cc. Fifty cc. of the liquid is mixed in a beaker with 5 cc. of formalin (about 40 per cent aqueous formaldehyde solution), and 10 cc. of 33 per cent sodium or potassium hydroxide solution, and the whole heated on a water-bath for a few minutes and then allowed to cool. The liquid is now neutralised with acetic acid, and the precipitated mercury collected and washed. Filter and precipitate are shaken with 100 cc. of water slightly acidified with acetic acid, and exactly 20 cc. of N/10 iodine solution until all the mercury has passed into solution as mercuric iodide, and the excess of iodine is estimated; 1 cc. of N/10 iodine = 0·01 grm. of mercury or 0·01355 grm. of mercuric chloride. —G. Adanti, *Boll. Chim. Farm.*, 1916, lv., 553; *Journ. Chem. Soc.*, 1916, cx., 579; *Journal of the Society of Chemical Industry*, Dec. 30, 1916, p. 1258.

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[*] Abstracts reprinted from the *Journal of the Chemical, Metallurgical, and Mining Society of South Africa*, May, 1917.

Separation of Lithium from other Alkali Metals.

The author makes use of alcohol and ether to precipitate sodium and potassium chlorides from an aqueous solution containing them together with lithium chloride. The mixed alkali chlorides are dissolved in a minimum amount of cold water, treated with 1 drop of concentrated hydrochloric acid, and 20 cc. of absolute alcohol added gradually. The sodium and potassium chlorides should come down in a uniform granular condition. Sixty cc. of ether is added, and the mixture allowed to stand for about five minutes, filtered through a weighed Gooch crucible, and the containing vessel thoroughly washed with a mixture of alcohol 1 part and ether 4 to 5 parts. The precipitate is well washed and the filtrate evaporated to dryness, and the residue treated with 10 cc. of absolute alcohol, if necessary warming to complete solution. Fifty cc. of ether and 1 drop of concentrated hydrochloric acid are then added, the mixture allowed to stand for half an hour, the precipitate collected in the same crucible as used for the first precipitate, washed with ether-alcohol mixture as before, dried, gently ignited, cooled, and weighed. The ether-alcohol solution of lithium chloride is evaporated on a steam-bath, the residue dissolved in water, treated with a slight excess of sulphuric acid, transferred to a weighed porcelain or platinum dish, evaporated on a steam-bath, and ignited. If charring occurs, the treatment with sulphuric acid and ignition are repeated. In an optional method for the lithium, the ether-alcohol solution is evaporated on a steam-bath, and the residue dried at 110° C. for fifteen to twenty minutes, treated with 5—10 cc. of alcohol, warming if necessary, the solution diluted with about 50 cc. of water, and filtered, if necessary, through a Gooch crucible. The acid solution is titrated with N/10 alkali, the chlorides precipitated as silver salt, and from the weight of the latter is deducted the amount corresponding to the hydrochloric acid determined by titration. If the total quantity of mixed chlorides is greater than 0·5 grm. proportionately larger quantities of solvents are necessary in the first precipitation, but more accurate results are obtained when the total chlorides do not exceed 0·5 grm.—S. Palkin, *Journ. Am. Chem. Soc.*, 1916, xxxviii., 2326; *Journal of the Society of Chemical Industry*, Dec. 30, 1916, p. 1273.

NOTE ON MEMBERSHIP OF GERMAN ACADEMIES AND SCIENTIFIC SOCIETIES.

The declaration of war by Germany against Russia and France was, it is known, received with enthusiasm by practically every section of the German nation. The Professors who form the backbone of the German Scientific Academies and Societies were prominent as a whole in arousing this enthusiasm. It is largely due to them that a belief was created in German minds that Germany was superior to other nations, and that in consequence it was only just and right that German power over other nations should be extended.

No German Scientific Academy or Society has, so far as we know, issued any protest against the many infringements of humanity and of international law which have been characteristic of the German conduct of the war.

We have just received a note from the Royal Society's Office in regard to the Society's Year-book for the ensuing year. The members of the Royal Society doubtless reprobate the action of the German Government in bringing on the war, and its methods of conducting it, as much as any other section of British folk. It seems, therefore, incongruous that Fellows of the Society should continue to announce in the Year-book of the Society, in "Who's Who," or elsewhere, their Membership of German Academies and Scientific Societies as an honour which they value. It seems more consistent with the actual state of affairs that such mention should be omitted.

Some Fellows of the Society have, we understand, already adopted this course, with a view to bringing home to German scientific men that learning and research cannot be divorced from public conduct. Others with whom we have spoken intend to do so. Our occupations have prevented us from obtaining the opinions of the Fellows generally, but as we believe that there is a widespread desire for common action, we venture to call attention to the matter. For ourselves, we intend to omit mention of German Academies and Societies.

W. M. Bayliss.
James Dewar.
David Ferrier.
J. N. Langley.
W. H. Perkin.
Ronald Ross.
C. S. Sherrington.
Ernest H. Starling.
William Crookes.

Nov. 3, 1917

THE NITROGEN PROBLEM AND THE WORK OF THE NITROGEN PRODUCTS COMMITTEE.*

The war has served to bring into special prominence the fundamental importance of nitrogen compounds, not only for munitions but also for agriculture.

Nitrogen is an essential constituent of practically all modern explosives, both of the so-called high explosives and of propellants. The manufacture of the vast quantities that have been called for by the present conditions of warfare has led to an unprecedented demand for various nitrogen compounds.

Nitrogen is also an essential constituent of all vegetation, and the world's production of food is becoming more and more dependent upon the utilisation of nitrogenous fertilisers. The world's consumption of such materials appears practically to double every ten years, and in 1913 had attained the large figure of 2,500,000 tons of Chile nitrate and about 1,400,000 tons of ammonium sulphate.

With the outbreak of war, the demand for explosives became of paramount importance, and the requirements of agriculture for the time being took a secondary position. The prospect of a world shortage of food, however, has served to bring the agricultural aspect of the problem again into the forefront. In this connection it is worthy of note that in 1898 Sir William Crookes, in a carefully reasoned statement, called attention to the possibility of a shortage in the wheat supply of the world and to the vital bearing upon this question of an adequate supply of nitrogenous fertilisers.

The researches of Sir William Crookes and the experimental work of Lord Rayleigh upon the fixation of atmospheric nitrogen by means of the electric arc, pointed the way to a method of utilising the unlimited supply of nitrogen in the air, and thus providing against the time when other natural sources of nitrogen compounds should have become exhausted.

The establishment on a very large scale during the past twenty years of processes for nitrogen fixation is one of the most striking electro-chemical developments of modern times. Special reference may be made to the arc process as used in Norway, the Haber or synthetic ammonia process developed in Germany, and to the cyanamide process for the manufacture of nitrolim from calcium carbide, as carried on in Norway, Sweden, France, Italy, Germany, and the United States.

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* Munitions Inventions Department.

In spite of the fact that the incentive to the commercial establishment of nitrogen fixation may be said to have originated in this country, no steps were taken in the United Kingdom to obtain nitrogen compounds other than cyanides synthetically. The ammonia recovered at gas-works and coke-ovens has constituted practically the only form of combined nitrogen produced in this country. During the war the command of the seas has hitherto enabled Great Britain to rely entirely upon importation for the whole of our supplies of nitrate of soda, the most important raw material of our explosives industry. The Central Powers, on the contrary, having been cut off from external supplies, were compelled to fall back upon their internal resources, with the result that nitrogen fixation processes, some of which were established commercially before the war, have been developed upon an enormous scale.

Formation of the Nitrogen Products Committee.

Soon after the formation of the Munitions Inventions Department in August, 1915, proposals for the fixation of nitrogen began to be received from inventors. These schemes were referred to the Chemical Inventions Committee of the Advisory Panel, but as they were isolated applications of the general problem and were of limited scope, they did not immediately lead to any definite line of policy being taken upon the question. The importance of the problem was recognised, however, and the attention of the Minister was directed to it from time to time in the monthly departmental reports.

The inauguration of the submarine campaign in February, 1916, and the grave menace to over-seas supplies of nitrates, emphasised the importance of taking action on the matter. At this opportune moment a memorandum on the Nitrogen Problem was submitted to the Department by the Faraday Society. Several conferences were held to discuss the steps that should be taken, and as a result, the Nitrogen Products Committee was constituted in the following June. Members of the Advisory Panel, representatives of other Departments of the Ministry of Munitions, and of the Government, and delegates of the leading scientific societies were invited to serve. The terms of reference were as follows:—

1. To consider the relative advantages for this country and for the Empire of the various methods for the fixation of atmospheric nitrogen from the point of view both of War and Peace purposes; to ascertain their relative costs, and to advise on proposals relevant thereto which may be submitted to the Department.
2. To examine into the supply of the raw materials required; *e.g.*, pure nitrogen and hydrogen, and into the utilisation of the by-products obtained.
3. Since some of the processes employed depend for their success on the provision of large supplies of cheap power, to ascertain where and how this can best be obtained.
4. To consider what steps can with advantage be taken to conserve and increase the national resources in nitrogen-bearing compounds and to limit their wastage.
5. To carry out the experimental work necessary to arrive at definite conclusions as to the practicability and efficiency of such processes as may appear to the Committee to be of value.
6. As a result of the foregoing steps, to advise as to starting operations on an industrial scale.

An important advance was made when the then Minister of Munitions, the Right Hon. E. S. Montagu, M.A., met the Members of the Committee on October 10, 1916. He assured them that the Government appreciated the importance of the Nitrogen Problem, and that he would do everything in his power to see that the recommendations ultimately made received the fullest consideration. At this meeting the veteran scientist, Sir William Crookes, was able to be present. At the same meeting the organisation of the Committee was completed, and the following Sub-Committees were set up:—Processes, Economics, Experiments, Power, and General Purposes.

At a later date another Sub-Committee was found necessary to deal with the question of coal distillation processes and the production and utilisation of power-gas. The Gas-Firing Sub-Committee was accordingly constituted. In all, the Committee and its Sub-Committees have held upwards of eighty meetings.

Nitrogen Fixation Research.

The necessity for research was evident from the outset, and the Department at once took steps for the organisation of a suitable research staff and the acquisition of a laboratory. Fortunately, the co-operation of the authorities of University College was secured, and a part of the new Ramsay Laboratory, at that time scarcely completed, was placed at the disposal of the Department.

The item placed first on the research programme was a complete investigation into the production of synthetic ammonia by the Haber process. This decision was influenced by the claims made for the process and by the commanding position it occupies in Germany, where the economic conditions as regards coal supplies and the comparative absence of water power are similar to those in Great Britain. Moreover, the almost complete lack of precise information concerning the commercial details of this process made it apparent that the research would present many unknown factors, and was therefore likely to occupy a considerable time.

Towards the end of the year, the Committee came to the conclusion that the ammonia oxidation process was well adapted as an emergency measure for securing quickly a considerable output of nitric acid or nitrates. Although already working with more or less success upon the Continent, the process had not at that time been operated in this country. A systematic investigation of the most recent developments of the process was therefore undertaken.

Many important problems have arisen in connection with the two main researches indicated above. Reference may be made to such questions as the most efficient and commercially practicable catalysts for the synthesis of ammonia and for ammonia oxidation, and the commercial preparation in bulk and at a sufficiently low cost of hydrogen of the high degree of purity required for the synthesis of ammonia.

On account of the formidable technical difficulties presented by the different problems, it was obvious that a research staff of considerable experience in all the recent developments of physical chemistry was needed for carrying quickly to a successful issue the work of the research programme. In the selection of the personnel, therefore, endeavour was made to obtain men possessed of special qualifications. The Department has been fortunate in securing a number of such men, with the result that the progress made has been more rapid than might have been expected under the present difficult circumstances. It may be mentioned that the chemist responsible for the research on the synthesis of ammonia had the advantage of having previously worked for some time on the problem at Prof. Haber's laboratory at Karlsruhe.

In December, 1916, when the research work was in its early stages, a demonstration and lecture took place at the Research Laboratory, and was attended by representatives of the Explosives Supply Department and of the War Office, and by delegates and members of other Government Departments and of scientific societies. The Minister of Munitions, the Right Hon. C. Addison, M.P., was unfortunately unable to be present. He had, however, displayed warm sympathy with the work of the Committee, and early in 1917 asked for practical recommendations to be submitted to him at an early date.

Interim Report of the Committee.

In view of the magnitude and complexity of the problem the Committee was unable immediately to present a complete report. Certain definite conclusions had been arrived at, however, and these together with recommendations thereon, were embodied in a unanimous Interim Report, which was submitted to the Minister of Munitions in February, 1917. The substance of the recommendations is given below.

(*a*) *By-product Ammonia.*—The importance of increasing the output of by-product ammonia for munitions and for agriculture was pointed out. Steps were indicated whereby an increase could be obtained from existing gasworks and coke-oven plants. It was also recommended that action should be taken to avoid the loss of ammonia known to be occurring in certain districts.

(*b*) *Ammonia Oxidation Process.*—The erection at the earliest possible moment of plant capable of producing in the aggregate at least 10,000 tons of nitric acid per annum from gasworks or coke-oven ammonia was recommended.

(*c*) *Cyanamide Process.*—The erection of a factory having an annual output of the order of 50,000 tons of cyanamide was recommended, the cyanamide to be utilised as such for agriculture or for the production of ammonia.

(*d*) *Synthetic Ammonia Process.*—The erection of a full-sized trial unit plant for the synthetic ammonia process was recommended.

The Minister of Munitions invited members of the Committee to meet him, and the recommendations of the Interim Report were discussed in detail. At the conclusion of this meeting the Minister appointed a small Executive Committee to supervise the action involved in giving effect to his decisions, and to report to him from time to time upon the progress made.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 1, 1917.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

“*Reflexion of Light from a Regularly Stratified Medium.*” By Lord Rayleigh, O.M., F.R.S.

The remarkable coloured reflexion from some crystals of chlorate of potash described by Stokes, the colours of opals, and of old decomposed glass, &c., lend interest to the calculation of reflexion from a regularly stratified medium, in which the alternate strata, each of constant thickness, differ in refrangibility. The higher the number of stratifications, supposed perfectly regular, the nearer is the approach to homogeneity in the light of the favoured wave-lengths.

A general idea of what is to be expected may be arrived at by considering the case where a single reflexion is very feeble, but when the component reflexions are more vigorous, or when the number of alternations is very great, a more detailed examination is required.

An important distinction reveals itself according to the relative values of the refractivity and thicknesses. In the one case a sufficient multiplication of the number of strata leads to complete reflexion; in the other case it does not.

“*Two Cases of Congenital Night-blindness.*” By Sir William Abney, K.C.B., F.R.S.

It was the aim of Prof. Watson and myself to examine, if possible, cases of congenital night-blindness in the laboratory to see if they would throw any light on some problems of colour vision. Knowing that one of our colleagues on the Board of Examination for Colour Vision had published papers of an exhaustive character on the subject of the heredity of congenital night-blindness, we applied to him for his aid in securing cases of this class of blindness. He, Mr. Nettleship, kindly secured two cases which figured in his pedigrees as being of the congenital type, and met them at my laboratory where they were examined spectroscopically. An interesting fact appeared that in their extinction of the different rays of the spectrum all light disappeared throughout the spectrum at the same moment that the colour vanished, and that the *colour* vanished to the normal eye at the same point that it did to the colour-blind. This pointed to the fact that the (fourth sensation I have called it) colourless part of the rays failed to give any sensation of light. As normal eyes see in a faint light with these colourless rays, it is to be presumed that the night blind owe their blindness in faint lights to the absence of certain retinal processes which the normal eyes possess.

“*Duration of Luminosity of Electric Discharge in Gases and Vapours—Further Studies.*” By Hon. R. J. Strutt, F.R.S.

1. The behaviour of jets of luminous gas flowing away from the region of discharge at a low gaseous pressure has been investigated, using the principal permanent gases, also mercury vapour.

In a transverse electrostatic field the luminosity is deflected, part of it in most cases going to the positive plate, and part to the negative.

But in hydrogen when the pressure is not very low, nearly the whole of the luminosity is deflected to the positive plate, a small part remaining undeflected. As the pressure is reduced, an increasing part of the luminosity goes to the negative plate. Similar results are observed in mercury vapour.

2. Further observations are recorded on these jets at higher pressures, arranging a spark discharge so that the gas can flow out from it through an orifice into a sustained vacuum. With hydrogen (condensed discharge) the exuded jet of luminosity, about 9 mm. long, shows the Balmer series. The discharge spectrum shows widened lines. These become narrow as the luminous gas emerges.

3. Nitrogen in the same arrangement, with an uncondensed discharge, shows a jet with periodic swellings similar to those observed by Mach and Salcher and Emden when a jet of compressed air, examined by the shadow method, escapes into the open. The wavelength agrees with that to be anticipated from their experiments.

4. This nitrogen jet luminosity is not to be confused in any way with active nitrogen. The time for which it endures is of quite a different order of magnitude, and the spectrum is essentially different.

“*Surface Reflexion of Earthquake Waves.*” By G. W. Walker, F.R.S.

“*Characteristic Frequency and Atomic Number.*” By H. S. Allen, D.Sc.

1. Simple relations are found to hold between the values of the product $N\nu$ for different elements (N being Moseley's atomic number and ν the characteristic frequency).

2. For 25 metals it is found that the product can be expressed in the form $N\nu = n\nu_A$ (n a whole number and ν_A a constant of value $21 \cdot 3 \times 10^{12}$ sec.$^{-1}$ approximately).

3. The same rule is obeyed in the case of certain non-metallic elements.

4. Similar results are found when the characteristic frequency is calculated from the elastic constants by Debye's formula. The value of n thus obtained is not in all cases the same as that deduced from the specific heats.

5. Application of the theory of probability shows that

there is but a small chance of the product $N\nu$ approaching so nearly to integral multiples of a constant frequency by a mere accident.

6. It is found that the atomic numbers of Moseley give better agreement with the proposed relation than do the atomic ordinals of Rydberg.

7. The empirical results are discussed from the standpoint of the Quantum Theory, and it is suggested that the integer n may be related to the number of electrons concerned in determining the crystalline space-lattice of the element in the solid state.

8. A relation similar in character is found to hold for certain electronic frequencies. In such cases ν_A must be replaced by $\nu_E = 3{\cdot}289 \times 10^{15}$ sec.$^{-1}$ (Rydberg's constant).

9. This relation is considered with reference to the maximum of the photo-electric effect, the limiting frequency of this effect, ionisation potentials, and thermoonic potentials.

"*Historical Note on a Relation between the Gravitational Attraction exercised and the Elastic Depression caused by Load on the Plane Surface of an Isotropic Elastic Solid.*" By C. Chree, F.R.S.

PHYSICAL SOCIETY.

Ordinary Meeting, October 26, 1917.

Mr. W. R. Cooper, M.A., Vice-President, in the Chair.

A paper, entitled "*On a Class of Multiple Thin Objectives,*" was read by Mr. T. Smith, B.A.

The objectives dealt with are cemented combinations of several thin lenses. Two kinds of glass only are employed, the odd elements being of one kind, say, crown, and the even elements of the other kind, flint. Such lenses may be regarded as combinations of achromatic cemented doublets, and formulæ are found for the aberration coefficients of such lenses in terms of those of a standard doublet when the geometrical conditions for the absence of air-gaps between the components are satisfied. Generally speaking, the results reached are that the outer surfaces are concerned with coma, and the internal surfaces with spherical aberration. In all cases the determination of a system to satisfy given conditions involves only the solution of a quadratic equation, and an algebraic method thus effects a solution in a fraction of the time involved in a trigonometrical investigation. Chromatic differences of first order aberrations are easily determined.

The application of the method is illustrated by a series of quadruple objectives which satisfy the ordinary conditions for telescope objectives. Diagrams show the variation of the curvatures with the different forms, the magnitude of the second order spherical aberration, and the chromatic differences of first order aberrations.

Discussion.

Prof. J. W. Nicholson congratulated the author on the increased simplicity which he had brought to some of these important problems. He thought a good case had been made out for the further numerical investigation of this type of objective, and hoped the author would let the Society have the results of such an investigation soon.

Prof. A. E. Conrady (in a communication which was read by the Secretary) said that the paper could not be regarded as of much practical value. No practical optician would think of constructing a telescope objective of four or more cemented components: even a triple objective is avoided whenever possible, as the technical difficulties are very serious when there are several cemented faces in a lens of considerable size, and he could not conceive of the necessity of such complication ever arising in small lenses for telescopes.

Mr. T. Smith said a very great deal of work would be involved in a systematic exploration of the properties of multiple lenses over the possible range of optical glasses, and the publication of such an extension could not be expected in a short time. He did not quite understand Prof. Conrady's point of view, which would be most deplorable if it were generally adopted by the optical industry; for it could only lead to utter stagnation. Obviously there were always difficulties in making a complex rather than a simple instrument; but difficulties must not be allowed to retard progress, and no investigation should be starved out because of them. Unless investigations are made it is impossible to say whether the advantages they may show are sufficient to compensate the attendant disadvantages. As a matter of fact, the question of employing quadruple objectives had actually arisen as a practical proposition in an instrument designed by a practical optician. In the particular case the optical conditions turned out to be unfavourable to the use of such a lens. Had it been otherwise there is no doubt it would have been employed, and any technical difficulties—which were not regarded as a deciding factor—would without doubt have been overcome. In Germany certainly, and in this country also, he believed, quadruple and even quintuple cemented objectives had been made.

A paper on "*The Radius of the Electron and the Nuclear Structure of Atoms*" was read by Prof. J. W. Nicholson, M.A., D.Sc., F.R.S.

The electron is usually regarded as a globule of electricity with a definite radius. This conception has proved valuable, but involves difficulties in connection with the nuclear structure of complex atoms. On the view that the electron consists of a region of strain in the æther such line constants should have some significance throughout the whole æther; which may, in fact, be in some manner cellular with these linear magnitudes involved in the specification of the cells, and therefore in any strained structure composed of them.

The electron would be regarded as a state of strain which for practical purposes is concentrated at its centre, rapidly diminishing outwards according to some very convergent law involving some line constant in its specification. By way of illustration the idea is worked out mathematically on the assumption that the strain varies as $e^{-\lambda r}$, on which hypothesis λ^{-1} is the "radius." It can be shown that the Lorentz formula for mass as a function of velocity can be obtained for this type of electron. The charge on the electron is regarded as a fundamental property of the æther, and is related to Planck's constant h.

Discussion.

Dr. H. S. Allan—There can be little doubt of the existence of a relation, referred to by Prof. Nicholson, betweed Planck's constant h and the charge of an electron e. The relation suggested by Lewis and Adams may be written:—

$$ch = \sqrt[3]{\frac{8\pi^5}{15}}(4\pi e)^2,$$

where c is the velocity of light. Taking Millikan's latest value for e $(4{\cdot}774 \times 10^{-10})$ and $c = 3 \times 10^{10}$, we find $h = 6{\cdot}558 \times 10^{-27}$. From his photo-electric experiments Millikan found $h = 6{\cdot}57 \times 10^{-27}$ within about 0·5 per cent, and in his latest table of fundamental constants he gives $h = (6{\cdot}547 \pm 0{\cdot}013) \times 10^{-27}$. Thus the agreement is within the limits of experimental error. All the principal radiation constants can be expressed in terms of e. The curious numerical relations between the primary constants of physics, to which attention was directed in my paper read before the Society in 1915, depend upon the above formula connecting h and e. On the lines suggested in Prof. Nicholson's paper it would seem as if most, if not all, of the important constants of nature may be referred to some fundamental property of the æther.

Sir Oliver Lodge (communicated)—I am much interested in Prof. Nicholson's ingenious plan for doing away with the definite boundary of an electron, and devising a mathematical scheme which shall enable us to regard it as a point-centre of strain decreasing exponentially in every direction without limit, so that the linear dimension associated with it shall be—like many time-constants—the distance at which the density is reduced to $\frac{1}{e}$ th of what it is at the centre. This plan, if it can be developed properly, seems to get over many of the difficulties about the coherence of parts of a charge, and about the extraordinary properties of a nucleus, which though, from some points of view, an extremely small and highly-charged unit, yet necessarily has a complexity which enables it to be disintegrated and fired off in fragments. The ready permeability or inter-penetrability without destruction, of Prof. Nicholson's conception of an electric unit, seems likely to diminish the difficulty of conceiving such a nucleus, and, on the whole, his suggestions seem to me helpful and valuable. I do not feel justified in saying more at the present time.

Prof. NICHOLSON, in reply, said it was of interest to see that Millikan's final value of *h* was practically equal to the first value that had been obtained for that constant.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, November 7, 1917.

Mr. A. CHASTON CHAPMAN, Past-President, in the Chair.

MESSRS. Charles V. Bacon and Kapilram Hardivram Vakil were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Kendall Colin Browning, M.A.; Henry Edward Cox, B.Sc. (Lond.), A.I.C.; Frederick William Edwards; John Monteath Guthrie; Frederick Thomas Munton, A.R.S.M.; Leonard Owen Newton; Ernest Walter Wright.

The following papers were read:—

"*The Reductase Test for Milk.*" By PAUL S. ARUP, B.Sc., A.I.C.

Comparison is made between the results obtained by Barthel and Orla Jensen's reductase test and those obtained by plate counts. Sources of error are considered, and it is concluded that errors of under estimation arising in the case of milks which have been kept at low temperatures and errors of over-estimation in the case of pasteurised milks, may be minimised by carrying out the test at 28—29° C. instead of 38—39° C. without altering the time standards on this account.

Attention is called to the importance of using the proportion of methylene-blue recommended by Barthel and Orla Jensen, which is found to be 1 part in 270,000 parts of milk.

"*Note on Jets for Burettes.*" By J. H. COSTE, F.I.C.

The ordinary burette graduated in 1/10 cc. is usually provided with a jet which will deliver drops of about 1/20 cc. The tolerance of error in burettes marked NP is much smaller than the size of the drop if less than 25 cc. is used for a titration. It is therefore impossible to use it so as to make the best use of the graduation unless a fine jet is attached. The dimensions of jets delivering small drops are given in this paper.

"*Analytical Examination of Acorns and Horse Chestnuts.*" By JULIAN L. BAKER and H. F. E. HULTON.

Chestnuts and acorns were prepared for analysis by peeling, grating, and drying at 55 ; they were then finely ground in a hand-mill.

The marked variation in the cane-sugar content may possibly be correlated with the degree of ripeness.

The diastase in the chestnut behaves like the diastase of an ungerminated cereal. No diastase could be found in the acorn either before or after germination.

Acorns or chestnuts with their full moisture content yielded, after hydrolysis with acid, from 11·5 to 12·7 per cent of alcohol, or 32 to 36 gallons of absolute alcohol per ton of nuts as collected.

	Peeled chestnuts.				Peeled acorns.	
	1.	2.	3.	4	1.	2.
Moisture	2·6	3·5	1·85	2·4	1·45	3·32
Ash	2·9	2·8	2·45	2·77	2·25	2·70
Matter extracted by ethylic ether (oil)	6·1	5·0	7·1	7·2	5·0	4·7
Protein (N×6·25)	9·8	10·8	7·25	7·62	6·65	7·5
Reducing sugars as dextrose	3·6	9·1	3·29	1·6	4·9	8·18
Cane-sugar	8·1	11·1	7·27	17·5	1·9	0·1
Starch (Lintner)	47·8	21·9	42·8	42·2	57·1	55·7
Starch (taka diastase)	38·4	15·2	39·0	38·2	44·3	43·40
Pentosans	4·75	—	—	5·44	3·2	—
Crude fibre	2·0	—	—	2·6	2·2	2·28
Matter soluble in cold water	34·9	48·4	32·56	36·2	13·2	17·24

NOTICES OF BOOKS

Artificial Dye-stuffs; their Nature, Manufacture, and Uses. By ALBERT R. J. RAMSAY and H. CLAUDE WESTON. London: George Routledge and Sons, Ltd. 1917. Pp. vi+212. Price 3s. 6d. net.

IN this book an outline is given of the nature and uses of the chief classes of dyes, and in view of the likelihood of the dyeing industry greatly increasing in magnitude and importance in England, the appearance of such a summary, written as far as possible in non-technical language, must be regarded as timely. A knowledge of the rudiments of dyeing will be a valuable asset in the future, and this book provides a good foundation on the subject and an introduction to the study of larger works. The process of distilling coal and coal-tar is first shortly described, and then the constitutions of the more important classes of dyes are discussed in turn. The preparation of artificial indigo is comparatively fully treated, with diagrams of the plant used and a clear scheme of the processes by which it is obtained. Some account is also given of methods of applying dyes, and allusion is made to their uses in bacteriological work and in photography.

Rules and Constitution of the National Association of Industrial Chemists. Published by the Provisional Executive Council.

THE National Association of Industrial Chemists which has just been formed has for its objects the economic, intellectual, and social advancement of industrial chemists and metallurgists, the promotion of the interests of its members by collective action, the furtherance of the interests of young chemists, and education. All men and women engaged in industrial chemistry and metallurgy who have attained the age of nineteen are eligible for full membership, and those under nineteen may become associate members. Local sections are to be formed, with the Sheffield branch as the parent local section. Application forms for membership, and copies of the provisional rules, &c., can be obtained (price 4d. post free) on application to Mr. N. H. Bacon, Bailey Street, Sheffield.

Royal Institution. - A General Meeting of the members was held on the 5th inst.; Sir James Crichton-Browne, F.R.S., Treasurer, in the chair. The special thanks of the members were returned to a Lady Member for an anonymous gift of £500, and to Richard Pearce, Esq., for a donation of £100, to the Fund for the Promotion of Experimental Research at Low Temperature.

CORRESPONDENCE.

SCIENCE, GERMANY, AND BLIND ALLEY OCCUPATIONS.

To the Editor of the Chemical News.

Sir,—Prof. Pope in his address to teachers at Regent Street Polytechnic, October 6, 1917, speaks of "young men going into blind alley occupations and leaving nothing behind, and made no contribution whatever to progress." I should be tempted to consider mine a blind alley occupation, for personally I have not found science remunerative or receive very much encouragement, but to me it has always been a great attraction marred by insufficient means to carry it on. Through many years of practical experience, experimenting, and improving, many openings for valuable research have from time to time appealed to me. I know how I would set about the problems and the great expense that would be entailed to carry out my ideas, which may or may not be successful. In any subject of experiment there is always the risk of uncertainty, but there are always compensating advantages, in that, knowledge equally valuable, secondary to the experiments, or applicable in other directions, may appeal to the trained mind always on the alert. That one fact has been the real secret of Germany's success in the scientific world; she has fostered it and helped all classes with equal opportunities. In this country you must show a successful financial ending before you get any encouragement at all. There should be institutions to encourage research here, for science, or rather the faculty of readily attaining it, does not only exist among the well educated, as many men of small education (literally) largely self taught, could easily prove. Some of us are, shall I say, "gifted" in some direction or another, our patents alone prove that, and one meets many splendid mechanics of no education, literally. Such men, regardless of "qualification," should have their chance; our Scientists of old were not always of high qualification, they were largely of the type to which I refer, and they should be made a valuble asset to the State. All of us not blessed with the instinct of making money out of every little thing undertaken; truly the Scientist's very nature of inventing for the common good makes him a most generous man, and therefore he should be protected from becoming the dupe of the financier or his grasping employer, as so happens in nine cases out of ten to-day.

There are thousands of businesses up and down the country starving for scientific knowledge so to speak; a chemist would be the most valuable asset to them, but he is regarded as an expense, and would not be tolerated by men who know very little of the technicalities of their own business. I do hope the war will have changed business men's opinion for the better in this direction. Few can appreciate what it is to work under such difficulties, endeavouring to make the principal see the scientific side of the subject as it relates to the interest of his business, whilst he has not the least sympathy or the rudimentary knowledge to grasp it.

Again, to have your work cut about and altered in such a way that they claim any originality there is left in it, or to have wily men in position pilfer your ideas and receive every credit for them. Many workers know only too well the truth of these last remarks. Improvements and suggestions there can always be upon your work, but I am speaking of when it is done with deliberate intention of depriving you of credit due. Many will say "surely not," but I know I am not alone in my experiences. Now, I would suggest that there be State Research Institutions, on the lines of giving monetary employment; the worker then can support himself, and moreover be satisfied in knowing that his productions would become State property, and that he *would be* "contributing something to progress and the welfare of the nation." Those who have research work at heart, I feel sure, require small but just recognition; let the worker place his application before a board of men thoroughly in sympathy with and able to recognise the value of research, not a Board of Philanthropists who may have no knowledge of the subject, but may have many prejudices and favours to exercise. The State as employer could provide suitable workers for the benefit of Research at works all over the country, and so secure for the common good justice which the worker seldom gets, by, say, a Royalty or other charge on all ideas produced and used by the works.

The subject could be enlarged upon by better hands than mine. That something will be done is the wish of one who has done some little research work unpaid.—I am, &c.,

"A Poorly Paid Works Chemist."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences. Vol. clxv., No. 10, September 3, 1917.

Classification of Nickel and Manganese Steels.—P. Dejean.—Steels containing less than 25 per cent of nickel and giving a critical-point at very different temperatures on heating and cooling are generally called irreversible, while those containing more than 25 per cent and giving practically the same critical-point on heating and cooling are classified as reversible. The irreversible steels may have very different properties. Up to about 10 per cent they are relatively soft, and consist of ferrite and perlite. Above 10 per cent up to 25 per cent they are hard and martensitic. The former are pseudo- or quasi-reversible, while the latter are truly irreversible. From 0 to 3·5 per cent of manganese the steels are perlitic and from 3·5 to 11 per cent martensitic, but in the neighbourhood of 3·5 per cent there is an intermediate region in which the steel consists of troostite and martensite.

No. 11, September, 10, 1917.

Sensitiveness of the General Method of Extracting Alkaloids from Water.—L. Lannoy.—The author used 200 cc. of water containing alkaloid, made it alkaline with sodium carbonate, and then extracted with chloroform. He thus found that it was possible to detect 0·0001 grm. of alkaloid, which is one part in two million. By the same method one part in four million of aconitine could be detected.

New Volumetric Method of Determining Molybdenum and Vanadium in Steels.—M. Travers.—Molybdenum can be determined by reducing MoO_3 by means of a titrated titanous chloride solution, the excess being determined in the usual way by means of ferric chloride. If the concentration of the molybdenum is below 0·05 grm. per litre and the liquid contains about 1 cc. of HCl per 100 cc., the reaction occurs according to the equation $2MoO_3 = Mo_2O_5 + O$. V_2O_5 is reduced by $TiCl_3$ to V_2O_4, and thus vanadium can be determined similarly in steel.

No. 12, September 17, 1917.

This number contains no chemical matter.

MISCELLANEOUS.

The Rational Method of Clay Analysis.—A departure from the usual method of conducting this analysis will adapt it to an estimation of the quartz and felspar constituents as well as true clay. Five grms. of air dry clay are heated with successive portions of sulphuric acid (1 : 3) for an hour or two on the water-bath, taken down until the acid fumes on a sand bath, and after dilution with water the contents are decanted through a filter, reserving the residue, which is treated once or twice with solution of caustic soda 1 per cent and sodium carbonate crystals 10 per cent in solution, again decanting, and finally washing on to a filter with dilute hydrochloric acid. The silica and quartz residue after the contents and filter have been dried, ignited, and weighed are treated similarly. The estimation of true clay by difference is achievable, and its analysis useful. The analysis of the quartz and felspar as well as of the decanted solutions is especially valuable, as the potash should be estimated in both.—J. C. Thomlinson, B.Sc.

Palladium-Gold Crucibles as Platinum Substitutes.—*Met. and Chem., Eng.*, 1917, xvi., 533; *Journ. Soc. Chem. Ind.*, 1917, xxxvi., 670.—An alloy of palladium and gold known as "Palau," which has been prepared as a substitute for platinum, has the surface colour of pure palladium, and is similar to, but slightly darker than hammered platinum. Tests at the U.S. Bureau of Standards showed that a crucible formed of the alloy is not so easily de-formed as one of pure platinum, though not so rigid as a crucible made of platinum with about 8 to 10 per cent rhodium. The sp. gr. of the alloy is 17·22 and the melting-point 1370° C. The E.M.F. against pure platinum is 8·5 millivolts at 960° C. and 7·2 millivolts at 860° C. A crucible of the alloy was heated to 1200° C., in a furnace free from metal vapours for two periods of four hours each, and weighed before and after each heating. The weighings to determine the loss due to heating were followed by treatments for five minutes with boiling hydrochloric acid (1HCl to $4H_2O$), and the loss in weight due to the acid treatment was determined. The solutions obtained from this crucible contained less than 0·01 mgrm. of iron. The tests indicated that the "Palau" crucible, as far as resistance to loss on heating to 1200° C. is concerned, is superior to platinum containing about 2·4 per cent iridium. The comparative freedom from iron is an improvement over most platinum ware now in use. The alloy compares favourably with platinum in resistance to hydrochloric, nitric, hydrofluoric, and sulphuric acids, ferric chloride, and sodium hydroxide solutions, and fused sodium carbonate. The "Palau" crucible is not as suitable for potassium pyrosulphate fusions as platinum. Both this alloy and platinum are seriously attacked by fused sodium carbonate and nitrate mixture, though in this case the "Palau" crucible is the more resistant.—*The Analyst*, xlii., No. 497.

British Industries Fair.—Next year's British Industries Fair, for which application forms for exhibiting space are now being issued by the Board of Trade, will be considerably larger than those of previous years. The last two Fairs were held in the Victoria and Albert Museum and the Imperial Institute, and, though wonderfully successful, the space which was then available was by no means sufficient to meet the demands of the exhibitors. In many cases, in fact, exhibitors' applications for space had to be cut down by as much as 60 per cent, and the fact of the Fair being in two buildings caused some inconvenience. The 1918 Fair, which will as usual open on the last Monday in February (February 25) and remain open for a fortnight, is to be held in premises which the Port of London Authority have been so good as to place at the disposal of the Board of Trade, and it is hoped that the available space will be sufficient to meet exhibitors' requirements, at any rate for this coming year, as the Fair will, owing to the war, again be restricted to the following trades:—Earthenware and China Trade; Glass Trade; Fancy Goods Trade; Paper, Stationery, and Printing Trades; Toy and Games Trade. The fact that the building for next year's Fair contains about twice as much space as the Board was able to secure at the Victoria and Albert Museum is only one of its advantages. In the first place, it is more conveniently situated for business men, being near the Tower Bridge and only a few minutes' walk from Mark Lane Station on the Metropolitan and District Railways, and, in the second, the building is exceptionally well suited for the purpose of the Fair, being a large roof-lighted warehouse on one floor. Some idea of its size can be gained from the fact that its area would be sufficient to accommodate two full-sized Rugby football fields. As in past years, invitations to the Fair will be issued by the Board of Trade, and admission will be restricted to bona fide buyers in the trades concerned. As the increased size of the Fair and the growing shortage of labour will make the work of preparation exceptionally difficult, it is hoped that firms who are anxious to exhibit will send in their applications for space to the Director, British Industries Fair, 10, Basinghall Street, London, E.C. 2, at the earliest possible moment.

MEETINGS FOR THE WEEK

Wednesday, 21st.—Royal Society of Arts, 4.30. "Science and its Functions," by A. A. Campbell Swinton, F.R.S.

—— Society of Glass Technology, 3.15. (In the Rooms of the Society of Chemical Industry, Queen's Hotel, Leeds). "Gas Firing and the Glass Industry," by Prof. J. W. Cobb.

Thursday, 22nd.—Royal Society. "Bactericidal Properties conferred on the Blood by Intravenous Injections of Diamino-acridine Sulphate," by C. H. Browning and R. Sulbransen. "The Pelmatoporinae—an Essay on the Evolution of a Group of Cretaceous Polyzoa," by W. D. Lang.

TO comply with Regulation 8 (*b*) of the Defence of the Realm Act, advertisements from firms whose business consists wholly or mainly in Engineering, Shipbuilding, or the production of Munitions of War, or of substances required for the production thereof, must include the words "No person resident more than ten miles away or already engaged on Government work will be engaged."

Assistant Chemist required for Works Laboratory situated in healthy hilly country. Used to all classes of Analysis. Ineligible for Military service. State full particulars as to qualifications, experience, salary required, &c. Permanency.—Address, "M. 371," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Assistant Metallurgical Chemists wanted to control Electric Steel Melting Furnaces. Preliminary training given. State age, full particulars of experience, salary required. No one fully employed on Government work will be engaged.—Apply, your nearest Employment Exchange, mentioning No. A. 4030.

Chemist seeks Engagement. Post with scope for organising ability preferred. Fifteen years' Laboratory experience; Organic and Inorganic Research, Foods and Drugs, Steels, Alloys, Plant Products, Tobacco, &c.—Address, "Ova," Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted, an Assistant Chemist. One accustomed to the Analysis of Oils, Soap, Feeding-stuffs, and Fertilisers, and ineligible for Military service. A discharged soldier preferred. Please state experience and salary required.—Address, Box 152, Morison's Advertising Agency, 74, Lowgate, Hull.

Women or Men Analytical Chemists required at salary of £150 per annum in Government Department, South of England.—Address, G. D., Chemical News Office, 16, Newcastle Street, Farringdon Street, London, E.C. 4.

Wanted, for Oil Refining and Hardening Works, TWO COMPRESSORS—one of 8000 cubic feet per hour and one of 24,000 cubic feet per hour; CONTROL APPARATUS, clock pattern; ELECTRICAL THERMOMETER for Catalyser; TWELVE 3-inch CENTRIFUGAL PUMPS; ONE BLOWER, 60 Centigrade water pressure; TWENTY-TWO TANKS—ten of 20 ton capacity, four of 15-ton capacity, eight of 10-ton capacity, the last to be wooden or lead-faced.—Write, with full particulars, to Box 429, care of Mather and Crowther, Ltd., 10-13, New Bridge Street, London, E.C. 4.

THE CHEMICAL NEWS

Vol. CXVI., No. 3026.

DISSOCIATION OF COMPLEX DOUBLE SALTS IN AQUEOUS SOLUTIONS.

By HAROLD L. MAXWELL.

The purpose of this work is to study the condition of double salts in aqueous solutions. Graham was the first to show that two sulphates could be separated by diffusion (*Am. Chem. Pharm.*, 1851, xvii., 56). This was confirmed by Marignac, who arrived at the conclusion that "double salts are formed only at the moment of crystallisation." In 1882 Rudorff made a study of the diffusion of some of the double chlorides and bromides. He diffused the double salt solution, using gold-beaters skin as a membrane (*Ber.*, 1888, xxi., 4), and then analysed the diffusate, and in this way determined the proportions in which the double salt came through. If the diffusate contained the various elements in the same proportions that they would be found in the double salt then the salts did not dissociate in solution, but if the elements were present in a different ratio from that found in the double salts, then it was plain that the double salts had dissociated in the aqueous solution. From these determinations it was possible to divide double salts into two general classes. First, those which suffer decomposition in aqueous solution, and, second, those which are not broken down when in a water solution. To the first class belongs :—

Copper potassium chloride ..	$2KClCuCl_2,2H_2O$
Magnesium potassium chloride	$KClMgCl_2,6H_2O$
Copper ammonium chloride ..	$2NH_4ClCuCl_2,2H_2O$
Sodium cadmium chloride ..	$2NaClCdCl_2,3H_2O$
Zinc potassium chloride . ..	$2KClZnCl_2,H_2O$
Barium cadmium chloride ..	$BaCl_2CdCl_2,4H_2O$

The following three double chlorides are not dissociated in the presence of water :—

Sodium platinic chloride . ..	$2NaClPtCl_4,8H_2O$
Potassium platinic chloride ..	$2KClPtCl_2$
Mercuric ammonium chloride	$2NH_4ClHgCl_2$

Later, some important work was done on these compounds and others by Kremers (*Pogg. Ann. Phys.*, 98), Grotian (*Wied. Ann. Phys.*, xviii., 177), Berthelot (*Ann. Chim. Phys.*, [5], xxix., 198). The latter gave us the general proposition, founded upon his thermo-chemical studies :—"Double salts formed with the liberation of a small amount of heat are to be regarded as separated, for the most part, into their constituents by water."

In 1910 Parsons and Evans made a valuable contribution to the study of double salts (*J. Am. Chem. Soc.*, xxxii., 1383). They made a study of the following double sulphates :—Ammonium chromium sulphate, potassium chromium sulphate, potassium aluminium sulphate, ammonium aluminium sulphate, ferric ammonium sulphate.

They came to the conclusion that :—"When alums are dissolved in water they are decomposed into the simpler sulphates which can be separated from each other by diffusion. The chromium alums separate more readily than do the aluminium alums."

Jones and Ota used the conductivity method in determining the presence of the double salts, and by increasing the dilution they were able to determine the rate of dissociation (*Am. Chem. Journ.*, xxii., 5). The work included the study of four double chlorides, and those at only a small range of dilution. The method was em yed by Jones and Knight in a comprehensive study of the double chlorides and bromides (*Am. Chem. Journ.*, Aug. 1899, xxi., No. 2). This work included many more double salts than had been studied before, and each one was measured over a much wider range of dilution. In several salts the dilution ranged from the molecular weight in 2 litres to the same in seventeen thousand litres. An important part of the work was the discovery of two new double bromides :—Sodium cadmium bromide and ammonium zinc bromide. These two salts were analysed and found to have the composition $2NaBr.3CdBr_2,6H_2O$ and $3NH_4Br.ZnBr_2$.

This work by Jones and Knight included the following four double chlorides and as many double bromides.

Sodium zinc chloride.
Strontium cadmium chloride.
Ammonium magnesium chloride.
Potassium magnesium chloride.

Barium cadmium bromide.
Potassium cadmium bromide.
Sodium cadmium bromide.
Ammonium zinc bromide.

Double Salts in Aqueous Solution.

The compounds which we have studied are :—Sodium cadmium bromide, ammonium zinc bromide, copper ammonium chloride, iron ammonium sulphate.

In the study of these compounds we used the diffusion method. We obtained the porous cups from Carl Schleicher and Schüll, and found that the size, 45 mm. wide and 100 mm. high, gave the best results. This article is listed as "Diffusions—Hülsen, No. 579." These cups are compact enough to admit diffusion only slowly, yet porous enough to pass enough material to admit of accurate analysis. They are placed in 200 cc. beakers, and 50 cc. of the 5 per cent solution of the double salt is placed in each one. Then distilled water is placed in the beaker until it reaches the same level in the beaker that the salt solution has in the diffusion cup.

These beakers must be kept at a constant temperature, as this factor plays an important part in determining the amount of material to pass through the porous walls of the cup. By varying the temperature at one concentration of the salt solution and then by varying the concentration of the salt solution at each temperature, it is possible to secure an endless list of data showing the effect of temperature and dilution upon the rate of dissociation of the salts.

The Double Bromide of Sodium and Cadmium, $2NaBr.3CdBr_2,6H_2O$.

We brought together the constituent bromides in the proportion two to three to form the salt $2NaBr.3CdBr_2,6H_2O$, which was first made by Jones and Knight and described in "Aqueous Solutions of Double Salts." The salt separated out in long narrow plates with tapering mitre-like ends. We dried the salt and made two analyses of it with the following results :—

Cd	32·60	32·77 per cent
Br	46·51	46·50 „
H_2O	21·00	20·90 „
Total ..	100·11	100·17 „

Since the total percentage of the elements of this salt was 100 it is evident that no sodium salt was present in the compound. By calculation we found that the results from the above salt corresponds to the formula $CdBr_2,4H_2O$, which has the percentage composition :—

Cd	32·56 per cent
Br	46·51 „
H_2O	20·93 „
Total	100·00 „

The cadmium bromide which crystallised out of this mixture of salts resembled the original cadmium bromide very closely, and when a microscopic examination was made of the two salts it was noted that the two were identical in crystalline form.

The cadmium bromide which we had obtained was returned and redissolved in the mother solution. More of the sodium bromide was added until the amount of the two bromides was proportional to their molecular weights. From this mixture there separated out a salt made up of small six-sided plates about the thickness of a ten cent coin. An analysis of this salt gave the following results:—

Cd	30·00	per cent
H_2O	10·09	"
Br	56·47	"

This corresponds to the formula $2NaBr.3CdBr_2,6H_2O$, which has the percentage composition:—

Cd	29·8	per cent
Br	56·59	"
H_2O	9·55	"

With this assurance that we had the right salt we proceeded with the diffusion tests using the method previously outlined. We made these tests at several temperatures, and also at different concentrations and time intervals, as follows:—

Concentration, 5 per cent.
Temperature, 13° C.
Duration of test, forty-five minutes.

We found on the analysis of the diffusate the following salt in the solution:—

	No. 1.	No. 2.
$CdBr_2$	0·04009	0·04131
NaBr	0·02290	0·02320

In the double salt crystals, the proportional parts of the various elements may be represented by the formula $2NaBr.3CdBr_2$. Since the molecular weights of these are 206 and 810 respectively, it is evident that if this salt does not dissociate in a water solution the two salts found in the diffusate would bear the same ratio to each other.

From the above molecular weight it is seen that the cadmium bromide should be 3·9 times heavier than the sodium bromide if the double salt has not dissociated. But we find from the analysis of the diffusate that the sodium bromide is little more than half the weight of the cadmium bromide that diffused through the porous cup:—

(5 per cent. 46° C. Forty-five mins.).

	No. 1.	No. 2.
$CdBr_2$	0·10053	0·10915
NaBr	0·04953	0·05244

In this we have less than half as much of the sodium salt as of the cadmium. It seems, then, that less of the salt has dissociated, since the ratio is more nearly 1 to 3·9. This may not necessarily point to the fact that the salts break down more easily in cool than in warm water. It may be that the heat has so lessened the internal friction of the solvent that it passes through the walls more easily and in carrying a greater amount of the solid matter in the same time the more cadmium was taken through.

(25 per cent. 13° C. Forty-five mins.).

	No. 1.	No. 2.
$CdBr_2$	0·12916	0·12480
NaBr	0·07610	0·07052

It is readily noted that the 25 per cent solution with the same time duration and the same temperature has diffused a much larger amount of the salt. We have found this true in each case with this salt.

(25 per cent. 13° C. Forty-five mins.).

	No. 1.	No. 2.
$CdBr_2$	0·13094	0·14458
NaBr	0·08861	0·0869

This test serves only to verify the foregoing one.

(2½ per cent. Room temperature. Twenty-four hours).

	No. 1.	No. 2.
$CdBr_2$	0·40921	0·36731
NaBr	0·19392	0·17313

We made an analysis of the contents of the porous cup also, and found that even in the twenty-four hours the solution had not reached its equilibrium; that is, the solution within the cup contained more of the salt per cc. than did the solution surrounding the cup within the beaker.

Sodium cadmium bromide dissociates when dissolved in water. The sodium bromide diffuses more rapidly than the cadmium bromide.

The Double Bromide of Ammonium and Zinc, $3NH_4Br.ZnBr_2$.

We added the ammonium bromide to the zinc bromide in the proportion 3 to 1 to form $3NH_4Br.ZnBr_2$. There separated out a large amount of crystals which we analysed with the following results:—

Br	77·09	per cent
Zn	12·60	"
NH_4	10·40	"
Total	100·09	"

This compares favourably with the calculated results which are:—

Br	77·07	per cent
Zn	12·52	"
NH_4	10·40	"
Total	99·99	"

With the use of the same method employed in the examination of the preceding salt we diffused this salt, and found the following results:—

(5 per cent. Room temperature. Twenty-four hours).

	No. 1.	No. 2.
$ZnBr_2$	0·43537	0·42142
NH_4Br	0·78583	0·77359

In the double bromide the ratio between the two constituent bromides is 1 of the zinc to 1·3 of the ammonium bromide. Unless it is dissociated by the water the diffusate should contain these elements in the same ratio one to the other. We find, however, on analysis that the ammonium bromide is much in the excess of this ratio. The results show that the ammonium bromide is in the excess bearing the ratio to zinc bromide of 1 to 1·8.

(2½ per cent. Room temperature. Twenty-four hours).

	No. 1.	No. 2.
$ZnBr_2$	0·30132	0·32412
NH_4Br	0·35455	0·37241

(5 per cent. Room temperature. Twelve hours).

	No. 1.	No. 2.
$ZnBr_2$	0·28568	0·31271
NH_4Br	0·83258	0·847815

It appears from these results that, during the first twelve hours, the ammonium bromide goes through the porous cup much faster than during the second twelve hours. In the twenty-four hour test the ammonium was not present in a large excess, but in this analysis of the twelve-hour test we find that the ammonium bromide is present in much larger proportions.

(5 per cent. 55° C. One hour).

	No. 1.	No. 2.
$ZnBr_2$	0·04428	0·04947
NH_4Br	0·263105	0·291901

This test also shows the presence of a larger proportion of the ammonium bromide. The raising from room temperature to 55° C. has also been an active agent of dissociation.

(5 per cent. 55° C. Fifteen minutes).

	No. 1.	No. 2.
$ZnBr_2$	0·02518	0·019722
NH_4Br	0·08336	0·08059

The data here recorded, in connection with the preceding one, gives an excellent example which shows how the amount of solid matter that diffuses through the cup per unit of time is greatest for the first unit of time, and becomes smaller and smaller as the solutions become more nearly in an equilibrium. It is noted that half as much of the salt was diffused in the first fifteen minutes as was diffused during the first hour. This rate of decrease for each succeeding period diminishes until with long duration of time tests, when the solutions are nearly saturated, the difference or the rate of decrease is indeed very small.

(5 per cent. Room temperature. Twelve hours).

	No. 1.	No. 2.
$ZnBr_2$	0·27178	0·33167
NH_4Br	0·805854	0 8322062

This test was made under the same conditions as one of the foregoing, and similar results were obtained, each serving to check the other.

(5 per cent. Room temperature. Six hours).

	No. 1.	No. 2.
$ZnBr_2$	0·12064	0·10240
NH_4Br	0·46180	0·47242

It may be noted when comparing this six-hour test with the twelve-hour tests that less than half as much of the zinc bromide was diffused, while more than half as much of the ammonium bromide came through the walls.

Conclusions.

Zinc ammonium bromide dissociates in a water solution.

Ammonium bromide will pass through a dialyser faster than will $ZnBr_2$.

Ammonium bromide is more affected by temperature than is zinc bromide.

Ammonium bromide dialyses much faster than $ZnBr_2$ at the beginning of a test, but the amount dialysed per unit of time decreases more rapidly when the time is lengthened.

Copper-Ammonium Chloride, $CuCl_2.2NH_4Cl,2H_2O$.

For this investigation we used the salt crystals furnished by the Baker Adamson Co. An analysis of this salt compared favourably with the calculated composition, which is—

Copper	22·89	per cent
Ammonia	12·97	,,
Chlorine	51·16	,,
Water	12·97	,,

(5 per cent. Room temperature. Five hours).

	No. 1.	No. 2.
$CuCl_2$	0·10365	0·08954
NH_4Cl	0·40470	0·37995

From the formula of the double chloride of copper and ammonium it is plain that the two salts have combined in such a way that the relative molecular weight is 134 for the copper chloride and 107 for the ammonium chloride. If the salt does not dissociate we will expect then to find the salts in the diffusate in the proportion of 1 of the ammonium chloride to 1·25 of the copper chloride. The analysis, however, shows the presence of about four times as much ammonium chloride as of the copper chloride.

(5 per cent. Room temperature. Two hours).

	No. 1.	No. 2.
$CuCl_2$	0·07820	0·06680
NH_4Cl	0·23149	0·20469

The ammonium chloride is still present in an excess, yet not so much as in the first instance.

(5 per cent. Room temperature. One hour).

	No. 1.	No. 2.
$CuCl_2$	0·05428	0·05015
NH_4Cl	0·10626	0·10690

From the results of the five, two, and one hour tests it is readily seen that the difference is less in the shorter time tests.

It is to be expected, then, that since the $CuCl_2$ diffuses at a more even rate that the ammonium chloride comes through very much faster during the first part of the test and decreases rapidly until the weight of the copper salt seems to approximate the weight of the ammonium salt.

(5 per cent. 63° C. Two and a-quarter hours).

	No. 1.	No. 2.
$CuCl_2$	0·16231	0·15929
NH_4Cl	0·35727	0·34984

With this rise of temperature it is noticed that the two salts are approaching a different ratio, and that the ammonium chloride has taken another marked increase. Instead of the ratio 1 to 1·25 we have the ratio of 1 to 2¼.

(5 per cent. 63° C. One hour).

	No. 1.	No. 6
$CuCl_2$	0·07259	0·08508
NH_4Cl	0·20596	0·20188

This test serves to verify the statement made above concerning the rapid diffusion of the ammonia during the first part of the tests. We have in this data more evidence to prove the decrease of the ammonium chloride is more rapid than the decrease of the copper chloride for each additional time unit. The ratio between the two salts for the shorter periods is higher than for the longer periods.

(5 per cent. Room temperature. Ten hours).

	No. 1.	No. 2.
$CuCl_2$	0·24141	0·26204
NH_4Cl	0·52293	0·51076

Iron-Ammonium Sulphate, $FeNH_4(SO_4)_2$.

(5 per cent. Room temperature. Two hours).

	No. 1.	No. 2.
Fe	0·01039	0·01249
NH	0·03608	0·04312

From the above formula we computed the ratio of the two constituent salts and found that they were present in the ratio of 100 of the iron to 33 of the ammonium sulphate. If, then, the salt did not dissociate, we would expect to find three times the weight of the iron sulphate as of the ammonium sulphate. But from the above data it is evident that the ammonium is much in the excess and that the double sulphate dissociates when in a water solution.

(5 per cent. Room temperature. Three hours).

	No. 1.	No. 2.
Fe	0·02548	0·01824
NH	0·05709	0·04244

We find here another example of how the ammonium salt decreases at a more rapid rate than iron salts for the longer periods.

(5 per cent. Room temperature. Five hours).

	No. 1.	No. 2.
Fe..	0·03998	0·04623
NH	0·07799	0·09438

The ammonium sulphate is still on the ratio decrease, and now, for the five hours' test, it is less than twice the the weight of the iron, while for the two-hour period it was three times greater.

(5 per cent, Room temperature. Ten hours),

	No. 1.	No. 2.
$FeSO_4$	0·08621	0·09196
$(NH_4)_2SO_4$	0·15411	0·16478

The total weight of the double salts which came through the walls during the ten hours' test is less than twice the weight of the salts which came through during the five-hour test. This is another example of how the total amount of the salt which passes through a dialyser during any period of time is greatest for the first period and decreases for each additional period. This is only to be expected, for as the solution within and without the porous cup come to approximate an equilibrium there is less pressure, and consequently less force urging the salts through the walls of the cup.

Conclusions.

The smaller ions diffuse more readily than the larger ions. Some ions, which are of themselves small, form hydrates, and thus becoming large diffuse as slowly as the large ions which do not form hydrates. This is in accord with the hydrate or solvate theory proposed by Jones and Knight.

We propose to investigate other complex salts and study their rate of dissociation in solvents other than water.

We desire to express our thanks to Prof. N. Knight for the assistance he rendered during the progress of this work.

Cornell College, Mount Vernon, Iowa.

ON THE QUALITATIVE DETECTION OF GERMANIUM AND ITS SEPARATION FROM ARSENIC.

By PHILIP E. BROWNING and SEWELL E. SCOTT.

Germanium, discovered in 1886 by Clemens Winkler (*Ber. Deut. Chem. Ges.*, xix., 210) is found in nature most closely associated with the elements silver, lead, mercury, cadmium, arsenic, tin, zinc, titanium, and niobium. Analytically it falls into the group with arsenic and tin, since its sulphide is precipitated in strong hydrochloric acid by hydrogen sulphide, and this sulphide dissolves readily in ammonium sulphide. The chief problem of separation, then, appears to be its separation from arsenic and tin. From tin, and antimony also if it is present, the separation is quite readily made by heating the sulphides with ammonium carbonate, which readily dissolves the germanium sulphide and leaves the tin and antimony sulphides practically unattacked.

Buchanan (*Journ. Eng. Chem.*, viii., 585) has quite successfully separated germanium from germaniferous zinc oxide containing lead, cadmium, arsenic, and traces of selenium, by dissolving this oxide in strong hydrochloric acid, distilling about one-half of the volume of the liquid, the distillation taking place in a current of chlorine gas in order to keep the arsenic in the higher condition of oxidation, and precipitating the germanium sulphide from the distillate by hydrogen sulphide.

The object of this paper is to give the results of some work upon the Buchanan method, and a simple modification of it devised for rapid qualitative tests.

Portions of zinc oxide (furnished through the kindness of the New Jersey Zinc Co.) containing germanium, amounting in all to about 425 grms., were distilled according to Buchanan's method, and about 1·45 grms. of germanium sulphide was obtained from the distillate, an amount which would be equivalent to a yield of about 0·24 per cent reckoned as the element germanium. This agrees closely with the percentage, 0·25 per cent, which the oxide was said to contain.

It was observed that the sulphide from the distillate obtained below the temperature of 108° C. had a slight yellow colour, indicating the probable presence of a trace of arsenic. The sulphide from the distillate coming over between 108° C. and 116° C. was in general much freer from arsenic, being practically pure white.

A simple form of apparatus was devised, consisting of a small flask fitted with a stopper through which a bent delivery tube passed into a test-tube, the end being just above about 5 cc. of water. The test-tube was then immersed in a beaker containing snow, ice, or cold water. As a substitute for the passing of chlorine gas a little potassium permanganate, manganese dioxide, or potassium chlorate was placed in the flask with about 10 to 15 cc. of strong hydrochloric acid and the germaniferous zinc oxide. The liquid in the flask was slowly brought to the boiling point, and about one-half distilled. By this method 1 grm., in another case 0·5 grm., of the oxide gave a distillate from which a heavy white precipitate was obtained with hydrogen sulphide—0·1 grm. gave a decided precipitate, and 0·125 grm. a noticeable trace. From these results it would appear that less than 0·0001 grm. of germanium can be detected by this procedure.

This method was applied successfully to a small sample of the mineral argyrodite previously decomposed by nitric acid, the product having been evaporated to dryness to remove excess of acid. The amount of germanium sulphide obtained from the weighed sample of mineral taken indicated the presence of about 8 per cent of germanium, which is very close to the percentage given for argyrodite. Five grms. of a leady residue from the purification of zinc, which had given spectroscopic evidence of germanium, gave a noticeable test for that element by this method.

To further confirm these results a solution of germanium sulphide in ammonium hydroxide was prepared, containing 0·001 grm. in a cubic centimetre, reckoned on germanium. Portions of this solution were used to determine the delicacy of the test, and it was found that 0·0001 grm. could always be easily detected, even in the presence of 0·2 grm. of pure ZnO, and 0·00006 grm. gave a satisfactory test when present with 0·025 grm. of ZnO.

1.	0·2 grm. $SnCl_2$ + 0·0005 grm. Ge ..	Reported Ge present; decided white precipitate.
2.	0·2 grm. $SnCl_2$ ..	Reported no Ge; very faint cloudiness.
3.	0·2 grm. As_2O_5 + 0·0005 grm. Ge ..	Reported Ge present; same as (1).
4.	0·2 grm. As_2O_5 ..	Reported no Ge; very faint cloudiness.
5.	0·2 grm. ZnO + 0·001 grm. Ge ..	Reported Ge present; decided white precipitate.
6.	0·2 grm. ZnO ..	Reported no Ge; not even cloudy.
7.	0·001 Ge	Reported Ge present; decided test.
8.	Distilled water ..	Reported no Ge; no cloudiness.
9.	0·1 grm. As_2O_3 + 0·0001 Ge	Reported Ge present; good test.
10.	0·2 grm. SnCl ..	Reported no Ge; faintly cloudy; no precipitate.
11.	0·0001 grm. Ge ..	Reported Ge present; good test.
12.	0·2 grm. As_2O_5 ..	Reported possible trace of Ge very faint.

A series of tests for germanium was prepared by one of us and given to the other, without the experimenter's knowledge of the substance present. The results are given in the accompanying table.

In all of these tests potassium permanganate was added with the hydrochloric acid before distilling, to provide the chlorine necessary to prevent reduction and distillation of $AsCl_3$ in the event of the presence of arsenic. Blanks were made with $KMnO_4$ to determine whether the chlorine evolved would cause a precipitate of sulphur in the distillate when hydrogen sulphide was added. The results of these determinations showed in only a few cases a faint cloudiness, probably due to sulphur, but in no case did a precipitate settle as in experiments where 0·0001 grm. Ge was present. Experiments (2), (4), (6), (8), (10), and (12) also showed that the use of potassium permanganate does not vitiate the germanium test. The distillates in Experiments (2) and (4) were allowed to stand over night after saturation with hydrogen sulphide without any precipitate separating from the very faintly cloudy solution.

Winkler (*Journ. Prakt. Chem.*, xxxiv., 177; xxxvi., 177, June, 1917) recommends the following method for the separation of germanium from arsenic. The sulpho salts formed by fusing the mineral containing the elements with sodium carbonate and sulphur are dissolved in water, and the solution is carefully neutralised with sulphuric acid, when the sulphide of arsenic is precipitated, leaving the germanium in solution. By treatment of this solution with hydrochloric acid and addition of hydrogen sulphide the germanium sulphide is thrown down.

Two modifications of this method were tried by us to bring about this separation. First, a solution of the sulpho salts was saturated with carbon dioxide. This treatment caused the precipitation of from 60 per cent to 75 per cent of the arsenic, while no germanium was precipitated. Second, a solution of the sulpho salts was treated with ammonium acetate, acidified with acetic acid, and then treated with hydrogen sulphide. Under these conditions the arsenic was completely precipitated, and the germanium remained in solution. This process was tried on solutions containing arsenic only and germanium only, as well as upon mixtures, with equal success. Finally, some solutions of content unknown to the experimenter were prepared by one of us, and the report by the other showed the accuracy of the method.—*American Journal of Science*, Oct., 1917.

THE NOMENCLATURE AND CLASSIFICATION OF THE NATIVE ELEMENT MINERALS.*

By EDGAR T. WHERRY.

In many respects it would be difficult to improve upon the nomenclature and classification of native elements worked out in Dana's "System of Mineralogy," yet with the advance of scientific knowledge new points of view are certain to arise and newly-discovered species to demand place in any scheme, so that changes must be introduced. A few suggestions in this direction are here put forward for discussion, criticism, or whatever fate they may seem to readers to deserve.

Nomenclature.

The names adopted by Dana are, as a rule, satisfactory, but wherever considerations of simplicity, consistency, and clearness suggest the desirability of changes from his usage, there should be no hesitation about introducing others.

When an element is known to occur in nature in but one form, no name different from that used for it in chemistry is needed; but several elements show polymorphous forms, and these have heretofore been distinguished by adding either a suffix (as in sulphur and sulphur*ite*), a prefix (as in palladium and *allo*-palladium), Greek letters as prefixes (as in α-sulphur and β-sulphur), or adjectives (as in *yellow* phosphorus and *monoclinic* selenium). The last method, using crystallographic adjectives, is preferable, because it can be employed alike in all cases, and its systematic introduction into mineralogical nomenclature is therefore recommended.

Many minerals consist of isomorphous mixtures of two or more elements. Two different methods of deriving names for these have been used in the past; first, by combining the names of the elements present, as selentellurium for selenium-bearing tellurium, platiniridium for platinum-bearing iridium, and nickeliron for nickel-bearing iron; and, second, by introducing arbitrary or special terms, as volcanite for selenium-bearing sulphur, sisserskite for iridium bearing osmium, and porpezite for palladium-bearing gold. As one element is almost invariably greatly in excess over the others, these should be regarded as varieties, rather than elevated to the rank of species. It is, further, believed to be highly desirable that species and varieties be distinguished by the terminology applied to them. As arbitrary or special names, including in this case the names of chemical elements, are generally accepted as appropriate for species, it is thought that their application to varieties should be discouraged, and such names as volcanite, sisserskite, and porpezite be discarded.

The use of chemical prefixes with species names in general is also objectionable, because of the resulting inconsistencies and ambiguities, as emphasised by Prof. A. F, Rogers (*Proc. Am. Phil. Soc.*, 1913, lii., 610); to this the native elements are no exception. For example, the mineral termed allemontite by Haidinger in 1845, a variety of arsenic containing a small amount of isomorphous antimony, has been called antimonarsenic by some mineralogists, and arsenantimony by others. When two diametrically opposed terms are thus applied to a single substance, it is evident that neither can be regarded as clearly expressing its nature, or accepted to the exclusion of others. Many other minerals, as amalgam, iridosmine, awaruite, &c., show similar confusion in their nomenclature.

To simplify matters and to make the terms as unambiguous as possible, the plan recommended by Prof. Rogers in the paper cited is favoured; that all varieties due to isomorphism be named by means of adjectives formed by adding the suffix *iferous* to the names of the elements present in smaller amounts (the names being put in the Latin form when necessary for euphony).

Classification.

In Dana's System the native elements are first split up into three divisions—non-metals, semi-metals, and metals. The first two divisions, however, show no pronounced differences, and various inconsistencies arise in apportioning the elements between them. For instance, graphite, which is classed as a non-metal, has a more metallic lustre and is a better conductor of electricity than arsenic, which is classed as a semi-metal. Selenium is regarded as a non-metal when monoclinic, and as a semi-metal when rhombohedral; and the same would have to be done with sulphur, arsenic, and antimony were all of their forms included, for these three crystallise in one or more forms with so-called non-metallic, and others with so-called semi-metallic properties. But the illogical character of this arrangement, which assumes that the element changes its fundamental nature on appearing in an unusual crystallised condition, is evident. The distinction between the non- and semi-metals appears, then, to be rather artificial, and both convenience and accuracy suggest that it be abandoned.

The major divisions are in turn sub-divided into groups. Throughout the greater part of Dana's System, the groups are composed of minerals of close chemical and crystallographic relationships. Among the elements, however, this arrangement is to some extent departed from, resulting in the establishment of a "carbon group," in which crystallographic similarity is lacking, and a "platinum group," which includes two types of csystallisation. As no good reason for this departure appears to exist, it is recommended that these groups be placed on a crystallographic basis. The carbon group then yields an isometric diamond group, into which several recently-discovered non-metallic elements fall, and a hexagonal-trigonal graphite group, which may for simplicity be united with the crystallographically identical arsenic group; in graphite $c = 1{\cdot}386$, which lies between the value for arsenic, 1·401, and that for antimony, 1·324; all three elements have basal cleavage.

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* From the *Journal of the Washington Academy of Sciences*, vii., No. 14.

Similarly, the platinum group may be split into an isometric and a hexagonal-trigonal group, while tin, which crystallises in a still different system, the tetragonal, is assigned to a group by itself.

In listing groups it is thought best to give those of the highest crystallographic symmetry first place, and to arrange the others in the order of decrease in symmetry.

A table of the native elements based on the above recommendations follows. Its criticism by anyone interested in the systematic arrangement of mineralogic data will be welcomed.

(To be continued).

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

Part II.—Liquids.

By IRVING LANGMUIR.

(Continued from p. 185).

Introduction.

The fundamental idea of the orientation of group molecules in the surfaces and in the interior of liquids as a factor of vital importance in surface tension and related phenomena, occurred to me in nearly its present form in June and July, 1916. During August surface-tension data for over 250 substances were tabulated and studied. Work on oil films began in June. As a result of this extensive work, clear ideas were obtained as to the orientation of molecules in the surfaces of liquids and the relation between the total energy $\gamma_0 = \gamma - T d\gamma/dT$ and the chemical constitution of such substances as benzene and its disubstitution products.

An account of this work was given in some detail in a paper read at the New York meeting of the American Chemical Society in September, 1916, and a short abstract was published in *Met. Chem. Eng.*, 1916, xv., 468. In this abstract only the more important conclusions were outlined, while the large amount of experimental data upon which these conclusions were based were, unfortunately, not given.

On October 27, at the Cleveland meeting of the American Physical Society, I described the mechanism of surface-tension phenomena, and presented the data for γ_0 for about 100 typical substances, and pointed out in detail the arrangements of molecules of benzene substitution products, especially indicating the effects characteristic of the ortho, meta, and para positions of a number of active and inactive groups. The bearing of this work on the hypothesis of the association of liquids was also pointed out.

Since this time I have found that Prof. W. D. Harkins has been developing an essentially similar theory of surface-tension phenomena. He has recently published two papers on this subject in the *Journ. Am. Chem. Soc.*, 1917, xxxix., 354 and 541.

Nearly all the data in the second of these papers (except, of course, the new experimental data presented), had been worked over by me during the summer of 1916, and it was my intention to publish them together with the material now given in the present paper. Dr. Harkness, however, kindly sent me advance manuscript of his papers, and I have therefore been able to avoid duplication of his work. Harkins had expected that his two articles would appear simultaneously, and as an unfortunate result he failed in his first article to mention my prior publication. In his second paper he refers to my work, but, by an oversight, fails to refer to the publication of my general results in *Met. Chem. Eng.*, although in the latter part of his paper (p. 584) he refers to this abstract in a footnote in which he points out that his conclusions regarding the orientation of the benzene molecules in the surface are the same as mine.

Under these circumstances it is desirable to quote a part of the abstract in *Met. Chem. Eng.*, 1916, xvi., 469, as follows:—

"A theory of surface tension is now proposed in which the structure of the *surface layer of atoms* is regarded as the principal factor in determining the surface tension (or rather surface energy) of liquids. This theory is supported in the most remarkable way by all available published data on the surface tension of organic liquids.

"According to this theory, the group molecules of organic liquids arrange themselves in the surface layer in such a way that their active portions are drawn inwards, leaving the least active portion of the molecule to form the surface layer. By 'active portion' of a molecule is meant a portion which is characterised by a strong stray field (residual valence). Chemical action may be assumed to be due to the presence of electromagnetic fields surrounding atoms. Surface tension (or surface energy) is thus a measure of the potential energy of the electromagnetic stray field which extends out from the surface layer of atoms. The molecules in the surface layer of the liquid arrange themselves so that this stray field is a minimum.

"The surface energy of a liquid is thus not a property of the group molecules, but depends only on the *least active portions of the molecules* and on the manner in which these are able to arrange themselves in the surface layer.

"In liquid hydrocarbons of the paraffin series the molecules arrange themselves so that the methyl groups (CH_3) at the ends of the hydrocarbon chains form the surface layer. The surface layer is thus the same, no matter how long the hydrocarbon chain may be. As a matter of fact, the surface energy of all these many different substances from hexane to molten paraffin, have substantially the same surface energy, namely, 46 to 48 ergs per sq. cm., although the molecular weights differ very greatly.

"If, now, we consider the alcohols such as CH_3OH, C_2H_5OH, &c., we find that their *surface energies* are *practically identical with those of the hydrocarbons*. The reason for this is that the surface layer in both cases consists of CH_3 groups.

"With such substances as CH_3NO_2, CH_3I, we find that the surface energy is much greater than that of the hydrocarbons. This is due to the fact that the volume of the I or the NO_2 is so great that the surface cannot be completely covered by the CH_3 radicals. The forcing apart of these groups increases the surface energy.

"Particularly interesting relations are found with benzene derivatives.

"In benzene itself, the group molecules arrange themselves so that the benzene rings lie flat on the surface, since the flat sides of these rings are the least active portions of the molecules. The surface energy of benzene is about 65 ergs per square cm.

"If now, an active group, such as OH, is substituted for one of the hydrogens in the benzene (forming phenol or carbolic acid) this group is drawn into the body of the liquid *tilting the benzene ring up on edge* and raising the surface energy to about 75 ergs per sq. cm., which corresponds to the activity of the perimeter of the benzene ring. Thus *any active group* strong enough to tilt the ring up on edge raises the surface energy to about 75. Two active groups side by side (ortho position) have no greater effect than one. But two active groups opposite one another (para position) cannot both go wholly below the surface, so that the surface energy then becomes abnormally large (about 85 in case of *p*-nitrophenol). The substitution of methyl or ethyl groups in the benzene ring lowers the surface energy except where an active group in an adjacent position draws these groups below the surface.

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* From the *Journal of the American Chemical Society*, xxxix., No. 9.

"Some of the best evidence in support of the new theory is derived from experiments on thin films of oil on water or mercury. Oleic acid on water forms a film one molecule deep, in which the hydrocarbon chains stand vertically on the water surface with the COOH groups in contact with the water.

"Acetic acid is readily soluble in water because the COOH group has a strong secondary valence by which it combines with water. Oleic acid is not soluble because the affinity of the hydrocarbon chains for water is less than their affinity for each other. When oleic acid is placed on water the acid spreads upon the water because by so doing *the* COOH *can dissolve in the water* without separating the hydrocarbon chains from each other.

"When the surface on which the acid spreads is sufficiently large the double bond in the hydrocarbon chain is also drawn down on to the water surface, so that the area occupied is much greater than in the case of the saturated fatty acids.

"Oils which do not contain active groups, as for example, pure paraffin oil, do not spread upon the surface of water."

In Part I. reasons have have been given for believing that all the forces acting between atoms (or group molecules) in solid bodies are fundamentally similar in character and are of the nature of so-called chemical forces. Thus, evaporation, condensation, solution, crystallisation, adsorption, surface tension, &c., should all be regarded as typical chemical phenomena.

Before proceeding with the application of this viewpoint to a consideration of the structure of liquids it will be profitable to examine more closely than heretofore the distinctions between this theory and the more usually accepted theory, according to which the above listed phenomena are manifestations of physical forces.

(*Note.*—In Part I. (Chem. News, cxvi., 60) the relationship between Werner's theory and the work on crystal structure was pointed out. The writer regrets that at that time he was not aware that P. Pfeiffer (*Z. Anorg. Chem.*, 1915, xcii., 376) had previously published a short paper discussing crystal structure from the viewpoint of Werner's theory. This has since been called to the writer's attention by Dr. G. McP. Smith. Even before the publication of Pfeiffer's paper, however, the writer had pointed out the application of Werner's theory to crystal structure in a paper read before the American Physical Society at Washington, D.C., on April 24, 1915, and an abstract of this paper was published (*Phys. Rev.*, 1915, vi., 79) a couple of weeks before Pfeiffer's article. The abstract contains the following reference to this subject:—"Bragg has shown that the atoms of crystals are arranged according to a space lattice, the identity of the molecules being lost. The forces acting between the atoms are thus chemical forces. In the case of diamond, the tetravalent character of carbon is manifest from the structure, but in most cases the valency appears to be *divided* between several atoms. Thus, in sodium chloride the single valency of the sodium atom is divided between six chlorine atoms. There is a close connection between this theory and Werner's theory of valence." R. B. Sosman, in a paper (*Journ. Ind. Eng. Chem.*, 1916, viii., 985) which appeared nearly simultaneously with Part I. of the present paper, has discussed the structure of silicates and other crystalline compounds from a viewpoint almost identical with that developed by the present writer).

"*Physical*" *versus* "*Chemical*" *Forces.*

When considering the action of forces between discreet particles in space, the physicist usually makes the simplifying assumption that each particle attracts or repels each other particle with a force which varies according to a function of the distance between the particles. Newton's inverse square law for gravitational attraction and Coulomb's law for the attraction or repulsion between electric charges are familar examples of such relations. Maxwell calculated the effect of temperature on the viscosity of gases on the assumption that molecules attract one another inversely as the square and repel inversely as the fifth power of their distance. Sutherland found that a formula in better agreement with the facts could be derived by assuming the molecules to be rigid spheres attracting one another with a force inversely as the nth power of the distance.

Van der Waals's equation of state for gases is based on the assumption that molecules attract one another according to some function involving only the distance between them. This method of derivation tacitly assumes that the forces do not depend on the orientation of the molecules, and further assumes that the force acting between any two molecules is not influenced by the proximity of other molecules.

J. E. Mills, in a series of papers on the subject of "Molecular Attraction" (a dozen or more papers on this subject have appeared in the *Journ. Phys. Chem.*) has advanced the theory that the only force acting between molecules in gases and liquids is an attractive force which varies inversely as the square of the distance between molecules.

Bakker (*Z. Physik. Chem.*, 1915, lxxxix., 1) has developed a theory of surface tension based on the assumption that the molecules of liquids attract one another according to an inverse exponential function of the distance. A somewhat similar theory of adsorption has been developed by Eucken (*Verh. Deut. Physik. Ges.*, 1914, xvi., 345).

These are only a few examples of the cases in which the forces between the molecules have been considered to be radial forces which vary solely as a function of the distance between molecules. In all the cases cited above the investigator has considered the phenomena to be physical in nature.

The chemist, on the other hand, in studying the properties of matter, usually employs totally different methods. He is often most interested in the qualitative aspects of a problem, and the quantitative relationships sought are usually limited to those deducible from the law of multiple combining proportions, the law of mass action, or the principles of thermodynamics. When the chemist does consider the forces acting between atoms or molecules, he does not look upon these as forces of attraction between the centres of the molecules, but he thinks rather of the specific nature of the atoms forming the molecules and the manner in which these atoms are already combined with each other. He thinks of molecules as complex structures, the different portions of which can act entirely differently towards any given reagent. Furthermore, he considers that the forces involved in chemical changes have a range of action which is usually much less than the diameter of a molecule, and perhaps even less than that of a atom.

Gurvich (*Z. Physik. Chem.*, 1914, lxxxvii., 323) distinguishes physical and chemical forces as follows:—

"I. *Physical Force of Attraction*—

(*a*) is not specific;
(*b*) has unlimited range of action;

(*c*) its action on a given mass is independent of the presence of other masses;
(*d*) it does not act atomistically; that is, it acts on masses as a whole and not along definite directions.

"II. *Chemical Force of Attraction* (*Affinity*)—
(*a*) is specific;
(*b*) its range of action is limited; probably to *atomic* distances;
(*c*) its action upon a given mass depends upon whether or not the force is already practically 'saturated' by other masses;
(*d*) it acts atomistically; that is, discontinuously in a few single rays or directions."

Gurvich considers that the forces involved in adsorption phenomena are not to be classed in either of these groups, but should rather be regarded as physico-chemical forces, as follows:—

"III. *Physico-chemical Force of Attraction*—
(*a*) is specific;
(*b*) its range of action is limited to molecular distances;
(*c*) its action upon a given mass is dependent on the presence of other masses;
(*d*) it is not atomistic, but acts as a whole without division into separate rays or directions."

The point of view developed in the present paper leads us to the following conclusions:—

A. Forces of the type which Gurvich has called Physical Forces do not play any important part in the structure of matter. The best examples of the physical forces are gravitation and the forces between electrically charged bodies. Gravitation is much too small a force to be of influence in holding atoms and molecules together. In all ordinary matter the negative and positive electricity are so uniformly distributed throughout the mass that the effective range of these electric forces is only of atomic dimensions.

B. *All* the interatomic and intermolecular forces involved in the structure of matter are chemical forces; that is, they are of the same nature as the forces that the chemist has been studying in the past. In general, these forces are of two kinds; those represented by primary and those represented by secondary valence. Adopting a scheme similar to that proposed by Gurvich, the characteristics of these forces are:—

IV. *Chemical Force* (*Primary Valence*)—
(*a*) is very specific;
(*b*) its range of action is limited to distances comparable to the diameters of atoms.
When several atoms are combined together by primary valence, however, certain effects may be transmitted from atom to atom over distances several times the diameter of atoms;
(*c*) its action depends entirely upon the degree of saturation of the atoms;
(*d*) it acts atomistically, in definite directions;

V. *Chemical Force* (*Secondary Valence*)—
(*a*) is moderately specific;
(*b*) its range of action is limited to atomic distances except where transmitted from atom to atom. The ranges of primary and secondary valences do not seem markedly different;
(*c*) its action depends on the presence of neighbouring atoms (Werner's co-ordination number), but not in such a definite way as in the case of primary valence;
(*d*) it acts only between adjacent atoms, but usually not in directions radiating out from single atoms.

In the great majority of cases, as has been shown by Werner, the distinctions between primary and secondary valence are well defined. Many cases of transition occur between the two, however, so that hard and fast rules should not be adopted.

The theory of valence recently advanced by G. N. Lewis (*Journ. Am. Chem. Soc.*, 1916, xxxviii., 762) seems to offer by far the most satisfactory picture of the mechanism of chemical combination that has yet been suggested. According to this theory the electrons in the outer shells of atoms tend to arrange themselves in groups of eight. There is also a very marked tendency for the electrons to group in pairs around positive charges. Thus, the stability of the hydrogen molecule and the helium atom is due to the existence of a stable pair of electrons. The neon atom contains an inner pair of electrons, with a stable group of eight electrons in the outer shell.

A carbon atom has four electrons in the outer shell. In the formation of methane the four electrons from four hydrogen atoms complete the group of eight. These eight electrons gather into four pairs, each of which holds one of the hydrogen nuclei in about the same way as the two nuclei are held together in a hydrogen molecule. In the molecule thus formed we cannot say that positively charged hydrogen ions are held electrostatically by a carbon atom with four negative charges. The eight electrons belong as much to the hydrogen nuclei as to the carbon atom. The chemical union is brought about by the electrons *held in common* by all the atoms. Thus, methane is a non-polar substance.

Similarly, the structure of carbon tetrachloride is accounted for, and it is readily seen why it too does not have a polar character.

When sodium and chlorine combine, the single outer electron of the sodium atom, together with the seven electrons in the outer shell of the chlorine atom, form the stable group of eight. In this case we have more reason to look upon the resulting compound as consisting of a negatively charged chlorine ion held by electrostatic forces to a positively charged sodium ion. Since the chlorine ion and the chlorine atom have radically different structures, however, it is not a useful conception to regard a chlorine ion as a charged chlorine atom.

This viewpoint leads us to a much clearer conception of the nature of primary and secondary valences.

Primary valence is the result of the tendency of the electrons to form groups of two or eight. (For the elements after the first two short periods it is evident that the electrons in the outer shell tend to arrange themselves in other ways than in groups of eight. We may expect, however, that Lewis's theory will soon be extended to cover these elements. Kossel's theory has made some progress in this direction). In the strongly polar compounds, electrons are transferred from the outer shells of the electro-positive atoms to the outer shells of the negative atoms in order to complete the stable groups of electrons. The primary valence relationships are dependent on the number of electrons that can be so transferred. In non-polar compounds, such as typical organic substances, a pair of electrons, held in common by two adjacent atoms, constitutes what we have usually represented by the single bond (primary valence).

When two or more atoms are thus combined by pairs of electrons held in common, there are still stray fields of force due to the electrons forming the outer shells of the atoms. Secondary valence is the result of these stray fields. The co-ordination number represents the number of groups which can arrange themselves in space around a given group. As was shown in Part I., a solid or liquid body (as, for example, a metal), may be built up of atoms held together exclusively by secondary valence.

From this viewpoint both primary and secondary valences are active in the formation of a crystal of sodium chloride. The transfer of the electron from the shell of the sodium atom to that of the chlorine atom involves primary valence. The two charged groups of electrons are then held together by their electrostatic fields to form the crystal (secondary valence). We thus see how, in a crystal, the arrangement of the atoms in no wise suggests the primary valence of the atoms, yet the chemical composition is in full accord with the ordinary rules of valence.

Not only Lewis's theory, but other recent theories of chemical valence, such as those of Stark, J. J. Thomson, and Kossel (*Ann. Phys.*, 1916, [4], xlix., 229), enable us to draw similar distinctions between primary and secondary valence.

Nothing definite is known regarding the forces acting on electrons inside of atoms. There seems to be increasing evidence that the electrons in atoms are not revolving in orbits around the positive nuclei, but should rather be regarded as stationary except when disturbed from their equilibrium positions by external forces. It may be, however, that a magnetic field (Parsons' theory) is to be associated even with stationary electrons in the atom. If this viewpoint is correct, we can no longer fall back on the convenient centrifugal force to explain why the electrons do not fall into the positive nucleus.

The writer believes with G. N. Lewis that Coulomb's law fails at short distances. From the internal structure of atoms we may, however, draw certain conclusions as to the nature of this failure. Since the electrons remain apart from the nucleus, it is evident that positive and negative charges repel one another when brought sufficiently near. The tendency of electrons to form stable pairs in atoms seems to indicate that two negative electrons (at least under the influence of neighbouring positive charges) attract one another when close together. Furthermore, it seems to be a reasonable hypothesis that an α-particle consists of *two* hydrogen nuclei (positive electrons) which nearly coincide, and therefore, according to the electro-magnetic theory, possess nearly four times the mass of a single hydrogen nucleus. In this case we would also conclude that two positive electrons, when brought sufficiently close together, attract one another and form the very stable α-particle.

From the viewpoint of these hypotheses, chemical combination by primary valence is the result of those as yet mysterious forces which cause electrons in atoms to be attracted together into pairs, or groups of eight.

The resulting molecules, or group molecules, have electrons arranged in definite ways in their outer shells. Thus, their surfaces should be looked upon as containing a large number of electric doublets, and probably also magnetic doublets. When two molecules are brought close together the doublets of one attract the doublets of the other, and result in the attraction between the two two molecules associated with the secondary valence.

It is evident, however, if we are to regard these secondary valence forces as being due to doublets, that we should not expect the force between the molecules to vary simply as a function of the distance, or to show other characteristics of the Physical Forces (I.) For example, let us consider the case of simple doublets such as bar magnets. One magnet attracts another with a force that depends primarily on the relative orientation of the two magnets. If two magnets come close together so that the north pole of one comes close to the south pole of the other the action of these magnets on a third has, in general, been greatly reduced. On the other hand, if the two magnets are placed end to end the attraction for a third may be greatly increased. These relationships are more nearly of the kind that we expect among chemical forces between atoms, rather than among physical forces such as those described by Gurvich. Thus from purely theoretical grounds, if inter-atomic forces are due to the presence of doublets, we conclude that all forces involved in cohesion, surface tension, &c., should come under the division of "Chemical Forces."

Nevertheless, the assumptions that have been made by van der Waals, Eucken, Mills, Bakker, &c., in their studies of the so-called physical properties of matter are not wholly unjustifiable. When molecules are separated by distances large compared to their diameters, under conditions such that all possible orientations occur with nearly equal probability, then it is evident that the *average force* between molecules will, for practical purposes, be a function solely of the distance between them. When, however, the molecules appproach so closely that they exert a marked orienting effect upon each other, then it is no longer justifiable any more than it was in the case of the bar magnets, to consider that the forces vary as a function merely of the distance.

The errors resulting from the assumption that the force varies solely with the distance become less important when we are dealing with atoms in which there are many doublets on the surfaces, and these doublets are uniformly distributed over the surface and are of small intensity.

In the case of the so-called permanent gases these conditions are fairly well fulfilled; also in so-called non-associated liquids there is a rough approximation to these conditions, so that certain useful results may be obtained by means of the simplifying assumption that the force varies as a function of the distance. However, such results should only be expected to hold in the case of molecules having *symmetrical* force fields and only when the distances between molecules is sufficiently great.

In the majority of cases such simplifying assumptions are not justifiable, and for this reason the formulæ derived often fail completely when applied to certain substances or over too wide a range of conditions. It will be shown in the present paper (Part III.) that the so-called associated liquids are merely substances which conform particularly badly with the customary simplifying assumptions. From the viewpoint developed in these pages such substances are in no wise to be regarded as abnormal. In other words, if we regard all the "physical properties" as resulting from chemical forces we are able to derive relationships which apply equally well to "normal" and to "associated" liquids.

The point that I wish to emphasise especially in the present paper is that such phenomena as cohesion, evaporation, crystallisation, adsorption, surface tension, viscosity, &c., apparently do not involve any inter-atomic or "intermolecular" forces other than the two kinds of force (IV. and V.) already familiar to the chemist.

The Relations between Solids and Liquids.

The differences between the properties of solids and liquids are much smaller than those between liquids and gases. The change in density in passing from the solid to the liquid state is insignificant in comparison with the change that occurs in passing from the liquid state to that of the gaseous (at ordinary pressures). Similarly, the compressibilities, coefficients of expansion, specific heats, refractive indices, and other optical properties, dielectric constants, and thermal conductivities of solids and liquids do not differ very materially in comparison with those of gases. For example, the similarity of solid and liquid mercury is in marked contrast to the great differences between liquid and gaseous mercury. In the gaseous state the mercury is colourless, transparent, and is a non-conductor of electricity, but the optical and electrical properties of solid and liquid mercury differ only slightly.

In fact, the only essential differences between liquids and solids seem to lie in the mobility of liquids and in those properties which are directly dependent on mobility. As a result of this mobility the definite lattice arrangement of the atoms of solids gives way to the irregular arrangements characteristic of liquids. The viscosity and the shearing elasticity of liquids are, of course, totally different from those of solids.

Surface tension is a property which we usually associate only with liquids. There is no doubt but that solids possess surface energy, and that the only reason that this does not manifest itself more clearly as a surface tension is that the solids do not possess sufficient mobility.

When a liquid shows electrolytic conductivity then the conductivity of the corresponding solid is usually much smaller because of the decreased mobility of the ions.

But where the conductivity is metallic there is ordinarily no great difference between the conductivities in the two states.

From these considerations, it is evident that the forces involved in the structures of liquids are not essentially different from those of solids. We may also reach this conclusion (as was done in Part I.), by arguing that amorphous and crystalline solids differ only as regards the regularity of the arrangement of their atoms, and by then considering that liquids may be obtained by a continuous process from amorphous solids, if we merely increase the mobility by raising the temperature.

If the forces holding solid bodies together are chemical forces represented by primary and secondary valence, then there is every reason for believing that chemical forces are also responsible for holding the atoms and group molecules of liquids together. Conversely, all the experimental evidence we find regarding the chemical nature of the forces within liquids may be considered as additional evidence in favour of a similar theory for solids.

The mobility of a liquid is thus due to a shifting of the relative positions of atoms which are all chemically combined with each other.

This mobility of atoms within the chemical molecule is nothing more than the familar phenomenon of tautomerism. In the field of organic chemistry this phenomenon has attracted considerable attention, because it seems to form such a marked exception to the behaviour of most organic compounds. As Lewis has pointed, however, tautomerism is an almost universal characteristic of inorganic substances (in the liquid state).

It seems probable that tautomerism occurs much more frequently in secondary valence unions than in those involving primary valency. It therefore occurs at the boundaries of the group molecules of organic substances rather than within these groups. The only solid body which seems to be held together exclusively by primary valence is the diamond (and presumably other forms of carbon), and this substance has never been obtained in the liquid state.

According to this viewpoint the viscosity of liquids depends upon the frequency with which tautomeric changes occur between the atoms or at the boundaries of the group molecules. This aspect of the theory will be considered again under the heading "Viscosity."

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 8, 1917.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

"*Galvanometric Measurement of 'Emotional' Physiological Changes.*" By Prof. A. D. Waller, F.R.S.

The principal object of this communication is to prove by demonstration that emotional response of the human subject is characterised (and can be measured) by alterations of the electrical resistance of the skin, independent of the well-known muscular and vasometer and secretory manifestations of emotion.

For this purpose there were projected upon the screen:—

1. On the upper scale the galvanometer spot, arranged to move to the + side with increased electrical conductivity due to emotional excitement (and returning to the − side with diminishing conductivity accompanying the subsidence of excitement).
2. On the lower scale the shadow of a delicate myograph to show the flucteutions of muscular contraction.

For the purpose of the demonstration, strong (disagreeable) stimuli are used, viz.:—

1. An unexpected loud sound (motor horn).
2. An unexpected burn (lighted match under hand, the striking of the match being, if possible, utilised as a warning signal).
3. A disagreeable pungent smell, under control of subject.
4. A painful thought, in some degree under control of subject.

For the purposes of accurate observation and measurement it is necessary:—

1. That the subject should be, as far as possible, quiescent and undisturbed by accidental excitation.
2. That the experimental responses should be recorded and signalled photographically by means of calibrated apparatus.

Demonstration of photograms selected from the records taken upon a chance series of 24 subjects (13 men, 11 women).

"*Structure, Evolution, and Origin of the Amphibia. Part I. The 'Orders'* Rachitomi *and* Stereospondyli." By D. M. S. Watson, M.Sc., Lieut. R.N.V.R.

In this paper all known genera of Rachitomous and Stereospondylous *Stegocephalia* are reviewed, the brain-case and basi-cranial region, hitherto practically unknown, being described more or less completely, and much new information about other regions set down. It is shown that there are a series of characters which change steadily with time in all *Labyrinthodontia*. The more important of these changes are:—

1. The gradual reduction and final loss of basi-occipital, basi-sphenoid, and supra-occipital bones and cartilages.
2. The gradual replacements of basi-pterygoid processes of the basi-sphenoid by expansions of the para-sphenoid, and finally of the ex-occipitals with which the pterygoids articulate.
3. The gradual increase in size of the inter-pterygoid vacuities and of the para-sphenoidal rostrum.
4. The gradual regression and final disappearance from the skull of a foramen for the hypoglossal nerve.

It is pointed out that these characters, which are seen to arise within these two groups, are those which have always been regarded as the diagnostic features of the class Amphibia, and that it is certain that they have arisen independently in at least three great orders.

Finally, it is shown that a hypothetical ancestor of the *Rachitomi* obtained by projecting backward the evolutionary trends shown in these and other series of characters which change regularly with time, is actually realised in the Embolomerous Amphibian *Pteroplax*.

"*The Enzymes concerned in the Decomposition of Glucose and Mannitol by* Bacillus coli communis. *Part II. Experiments of Short Duration with an Emulsion of the Organisms. Part III. Various Phases in the Decomposition of Glucose by an Emulsion of the Organisms.*" By E. C. Grey.

By selection, Harden and Penfold obtained evidence that the proportion in which the enzymes of bacteria occurred could be artifically modified, which result might suggest that the enzymes, although intracellular, are able to act independently of one another. The present researches demonstrate that this is a fact.

The results recorded in Part II. show that with the same bacterium the proportion between the products varies with the conditions, and in Part III. that during various periods of the life of the bacterium there are varying chemical changes, namely, (1) a period of carbohydrate synthesis co-incident with rapid multiplication, (2) transformation of synthesised material into lactic acid, (3) formation from carbohydrate of alcohol and acids (acetic, formic, succinic), accompanied by rapid death of the organisms. The extent of the synthesis of glucose into more complex carbohydrate is quantitatively of the same order as the subsequent degradation.

The increased production of alcohol during the rapid death of the cells recalls the view held by Pasteur that alcoholic fermentation was a pathological process.

The most important result is the demonstration of the magnitude of the synthetic side of the process of fermentation of carbohydrates by bacteria, and, in the second place, the proof that the fermentation can proceed in alternative ways according to the conditions, and hence that the sugar-splitting enzymes are able to act independently of one another.

The work suggests a new technique for bacterial chemistry. The bacteria are grown apart from the substance the fermentation of which is to be studied, and thus the chemical products of fermentation are not confused with others which might arise from the nitrogenous substances hitherto added in such experiments. A definite weight of bacteria is used. The duration of the experiment has been reduced from weeks to hours.

Approximately 1 grm. of bacteria (*B. coli communis*) will decompose 1 grm. of glucose in one hour.

SOCIETY OF CHEMICAL INDUSTRY.

Ordinary Meeting, November 5, 1917.

The following paper was read :—

"*Patent Law and British Chemical Industry.*" By Dr. F. W. Hay, Patent Expert of British Dyes Ltd.

In view of the fact that the prosperity of the country depends so largely on industrial activity and that no industry can maintain its reputation in the markets of the world without constant improvement, the question whether the inventive talent of the people is stimulated and assisted in every respect is a matter of primary importance. Dr. Hay pointed out that we have a fairly highly developed patent system in this country, the governing principle of which dates back to the Statute of Monopolies of 1623, and is still on a sound basis, but it has never been made to produce its full beneficial effect.

According to this governing principle of our Patent Law a patent in order to be valid should cover a new invention. The Patent Office, however, owing to the inadequate system of preliminary examination allotted to it by the Act of 1902, merely examines whether the invention to be covered by a patent is new with regard to prior British patents of the last fifty years. These British patents only represent a fraction of the industrial development that has taken place, as so many discoveries are made in other countries. Owing to this very incomplete system of examination patents issued in this country cannot be considered to contain any reliable evidence of novelty. Those that are granted for genuine inventions are inundated by a large proportion of patents delivered for inventions that are new only as far as prior British patents are concerned, but are not in fact entirely new. The Law, however, stipulates, and rightly so, that the invention should be new in every respect ; hence a serious anomaly exists between the attitude of the courts, which consider all prior publications, and that of the Patent Office, which examines prior British patents only. A patent sealed by the Patent Office is therefore liable to be upset in Court on the grounds of anticipation as soon as it is issued. The inventor finds it exceedingly difficult to introduce his invention owing to the lack of consideration given to patents in this country, and the manufacturer is deterred from using a new invention because the patent he is offered may or may not be a valid instrument of defence against infringers.

Recognising these conditions Dr. Hay expressed the view that it does not seem expedient to leave the novelty of the invention to be determined by the Courts. The novelty of all inventions to be protected by patents should, he considered, be investigated by the Patent Office by means of a *general system of examination*, covering all prior British and foreign publications. Without demanding any particular standard of novelty or applying the criterion of a "new practical effect" adopted in Germany, patents should be granted only for inventions that contain some novel feature over and above the inventions disclosed in the prior publications. All other applications for patents should be refused.

In addition specifications relating to Chemical Industry should, whenever the invention seems problematical or obscured by irrelevant or misleading statements, be verified by skilled chemists in suitable laboratories, so as to avoid the delivery of patents that are intended to obstruct. The supply of samples is deemed insufficient for this purpose.

It was further proposed that the public should be allowed five years within which the patent could be revoked on the grounds of anticipation, inadequate description, or prior use, and the validity of the patent should then no longer be open to attack in Court, so as to give greater security to any new manufacturer depending on patent rights.

The Courts find great difficulty in dealing with litigation relating to Chemical Industry, and frequently fall into serious scientific error. The Judge has to rely on expert evidence which he is unable to understand, because years of scientific training are required to be able to cope with the highly technical evidence brought forward. No demonstration *ad oculos* can, as a rule, be made. Great uncertainty therefore prevails with regard to patent litigation relating to chemical manufacture, and even wealthy companies often prefer to put up with a certain amount of infringement rather than defend their rights. To meet this difficulty Dr. Hay proposed that all actions in Court connected with infringement of patent rights should be tried in the presence of a "Technical Jury" consisting of experts engaged in the industry or science to which the action relates, and assembled in the manner of a "Special Jury," the Judge being required to submit the issue of infringement to the Jury.

NOTICES OF BOOKS.

Allen's Commercial Organic Analysis. Vol. IX. Edited by W. A. Davis, B.Sc., A.C.G.I. Fourth Edition. London: J. and A. Churchill. 1917. Pp. xviii+836. Price 30s. net.

This volume completes the fourth edition of "Allen's Commercial Analysis," and brings up to date the preceding eight volumes, which have been issued at intervals during the last eight years. The plan of issuing such a supplementary volume has many advantages, and the ninth volume is not the least valuable part of the treatise. The articles in it have mostly been written by the original contributors, and give summaries of the literature which has been published in the last nine years and of recent research work on analytical methods. The errata in the original volumes are tabulated, and a complete general index is provided. It is possibly unnecessary to allude to the many excellences of this treatise, which has been thoroughly tested and proved by analytical chemists of all nations, and it will be sufficient to say that this volume in no way falls below the level of its predecessors.

Molybdenum : its Ores and their Concentration. By Frederick W. Horton. Washington : Government Printing Office. 1916. Pp. vi+132. Price 30 cents.

The molybdenum industry is showing rapid development, and it does not appear unlikely that molybdenum in the future will compete with tungsten in the manufacture of steels. The object of this bulletin is to make accessible reliable information on methods of extracting the metal from its ores, its properties and quantitative determination. Its uses are also discussed, with special reference to the manufacture of steels, and it is pointed out that its uses have been greatly extended since the discovery of processes for drawing it out into wires. Thus it has found application in electric resistance furnaces, being much cheaper than platinum and superior to it in that it becomes hot more quickly, and the temperatures attainable are higher. The second part of the monograph deals with the distribution of molybdenum ore deposits in six of the western and Pacific Coast States. The large low-grade deposits of molybdenite and wulfenite which occur in these regions were thoroughly investigated with a view to their commercial possibilities, and detailed information relating to them is tabulated. Finally, methods of concentrating low-grade ores are described in full, with some discussion of costs and output.

CORRESPONDENCE.

ESTIMATION OF FREE SULPHURIC ACID.

To the Editor of the Chemical News.

Sir,—The difficulties which Mr. Naucollas has encountered in estimating free H_2SO_4 in the waste water he mentions may, I think, be overcome by the cautious addition to the measured solution before titration of a small quantity of "hypo." solution. A change of colour will probably be observed, and the addition of "hypo." should be continued, with agitation, until this ceases.

The solution may then be titrated, using methyl-orange as indicator.

Whilst the "hypo." solution can be quite strong—saturated if desired—it is undesirable to add too large an excess, as precipitation of its sulphur may occur (especially in a strongly acid solution), which would, of course, tend to mask the end reaction.—I am, &c.,

Harry V. Hodgson.

59, Dornton Road, Balham, S.W. 12,
November 19, 1917.

MISCELLANEOUS.

The Nitrogen Problem.—We regret to announce that the part of the pamphlet on "The Nitrogen Problem" issued by the Ministry of Munitions was printed in the Chemical News without permission, and, consequently, the continuation of that inserted on p. 240 must not be printed. We are glad to say that some description of the work of the Nitrogen Products Committee will probably be issued to the press, and the Comptroller will supply us with an advance copy of this matter, so that readers of the Chemical News may be in possession with the fullest information compatible with official requirements.

Compound Fertilisers Order.—The Minister of Munitions, in exercise of the powers conferred upon him by the Defence of the Realm Regulations, and of all other powers enabling him, hereby orders that the provisions of the Order relating to Compound Fertilisers made by the Minister of Munitions on October 13, 1917, shall, as on and from November 17, 1917, apply to sales of Compound Fertilisers for export from the United Kingdom to the Isle of Man, and that Clause 8 of the said Order shall as on and from the said date be modified accordingly.

Royal Institution.—Prof. J. A. Fleming, D.Sc., F.R.S., will deliver a Christmas course of six illustrated lectures (adapted to a juvenile auditory) on "Our Useful Servants—Magnetism and Electricity." The dates and subjects are as follows:—Thursday, Dec. 27, 1917, "Magnets and the Magnetic Compass"; Saturday, Dec. 29, "Electricity and Electric Currents"; Tuesday, Jan. 1, 1918, "Electric Current as a Heater and Chemist"; Thursday, Jan. 3, "Electricity as an Illuminator and Doctor"; Saturday, Jan. 5, "Electric Dynamos, Motors, Transformers, and Railways"; Tuesday, Jan. 8, "Electric Telegraphs and Telephones." The lecture hour is three o'clock. Subscription (for Non-Members) to this course, one guinea (juveniles, under sixteen, half-a-guinea); to all the courses in the Session, two guineas. Tickets may now be obtained at the office of the Institution.

The British Barimar-Thermit Welding Co., Ltd.—The Board of Trade have now given formal sanction to a new company, with works in London and Liverpool, and known as The British Barimar-Thermit Welding Co., Ltd., to take up and exploit the thermit welding process which, prior to the war, was exclusively in German hands. Thermit is especially applicable for tramway welding and for the repair of heavy castings and machine parts, and it is the intention of Mr. C. W. Brett, the Managing Director and General Manager of Barimar Ltd., Scientific Welding Engineers (who is largely responsible for the formation and management of the new company), to train disabled British soldiers and sailors to carry on the work. The registered offices of the new Company are at 10, Poland Street, London, W. 1.

Royal Institute of Public Health.—The following notice of postponement of Harben Lectures, previously announced for November 26, 27, and 28, has been received:—The Secretary begs to announce that a cablegram has been received from Dr. Alexis Carrel, who was to have delivered the Harben Lectures at the Royal Institute of Public Health on the above-mentioned dates, stating "Official demands keep me in America; please postpone lectures. - Carrel"

Encouragement of Science.—A recent instance of the methods by which technical science is encouraged (?) in this country is furnished by a correspondent of the *Yorkshire Observer*, who refers to the case of a young man, holding the B.Sc., M.A., and LL.B. degrees, who offered his services to a manufacturing company. He is teaching physics and higher chemistry, yet the British manufacturing company was unable to find him a position except at a salary of not more than £5 per week.—*Oil and Colour Trades Journal.*

British Industries Fair, 1918.—As certain Trade Associations connected with trades eligible to participate in the British Industries Fair, 1918, have until recently been unable to hold meetings to discuss concerted participation, and in order to suit the convenience of a section of the trade press, the Board of Trade have decided to extend the final date for the receipt of applications for space until November 30. The difficulties of organisation due to the war make it of the highest importance, however, that all applications should be sent in to the Director, British Industries Fair, 10, Basinghall Street, London, E.C. 2, at the earliest possible moment. The applications for space so far received from manufacturers point to the coming Fair being greatly increased both in size and importance.

Paper from Spent Bark.—The *Leather World* draws attention to a new use for spent wattle bark. It appears that the Imperial Institute authorities are highly satisfied with the result of tests, undertaken in the Institute laboratories, concerning the suitability of Natal wattle bark (after it has been discarded by the tanners) for the manufacture of paper. These tests, which were on a small scale, demonstrated that a good quality brown paper can be manufactured from the spent bark. This paper bleaches readily to a cream tint, and has been pronounced eminently suitable for newspaper purposes, and, with further treatment, may make serviceable writing paper. The Institute authorities have interested several large paper-mills in these discoveries, and large-scale tests are now proceeding to confirm the experiments on a commercial basis.—*Journal of the Royal Society of Arts*, Nov. 9, 1917.

MEETINGS FOR THE WEEK.

Monday, 26th.—Royal Society of Arts, 4.30. "Land Settlemen within the Empire," by Lieut.-Col. the Hon. Sirt John McCall, M.D., LL.D.

Wednesday, 28th.—Royal Society of Arts, 4.30. "Aerial Transport after the War," by G. Holt Thomas.

THE CHEMICAL NEWS

Vol. CXVI., No. 3027.

VARIABLE ATOMIC WEIGHTS,

With some Reference to Geologic Time.

By H. S. SHELTON.

The present short article arises out of a discussion held at the Geological Society two years ago. In that discussion I expressed the opinion that the hypothesis of variable atomic weights was contrary to the general trend of chemical knowledge, and that it was not probable that the determination of the "lead" in a mineral would give a clue to the origin of that constituent. That point, a minor one in the discussion, I must present to my opponent, Mr. Holmes (see note at end of article). Whatever conclusions Prof. Soddy's theory of isotropes may eventually lead to, he and Prof. Richards seemed to have fully proved that the end product of uranium differs in atomic weight from that of thorium, and that both differ in atomic weight from ordinary lead. It will, however, be of some service to show in what way the hypothesis of variable atomic weights seems to me to be unsound, and how Prof. Soddy's theory of isotropes, whether or no it is true in all respects, is not open to the more obvious objections to the general theory. Moreover, as Prof. Soddy's recent address, published in this journal, contains some remarks on geologic time, and apparently gives the weight of his authority to controversial views on a subject concerning which his opinion is hardly as valuable as is his study of isotropes, that aspect also calls for brief comment.

It will be convenient, first, to state the general objections to variable atomic weights. This idea, not, I believe, entirely unknown to chemical theory, postulated that the atoms of a chemical element, which chemical element was supposed to be in the mass in all respects homogeneous and inseparable, might vary in weight largely and symmetrically about a mean, the mean being the "atomic weight" of the element. This concept has always appeared to me, and also to others, as fundamentally unsound. In so describing it I am not merely thinking of obvious objections such as the possibility of separating the molecules of lighter mass by diffusion. I am raising a demurrer on principle against the idea that a hypothetical definite structural entity the atom, to which the properties of the element are referred, should vary in structure without also thereby varying in properties. Such a hypothesis appears self-contradictory. If the atoms be regarded as entities varying symmetrically about a mean, so must the properties referred to the atom.

At the time of the discussion at the Geological Society I had not seen Prof. Soddy's original paper (Chemical News, cvii,, 97), and even on reading it subsequently I was not quite sure that his hypothesis was not open to these objections. I had, indeed, partially written a paper mentioning such matters as density and diffusion. Moreover, the original paper appeared to me to postulate far too absolute a degree of inseparability, more than was warranted either by valid theory or by fact. The last objection still holds, but recent developments have rendered the others inapplicable. Prof. Richards's discovery of the variation of the density and the constancy of the atomic volume, and Prof. Soddy's recent suggestion of the possible separability of isotropes by diffusion, show clearly that the isotropes are neither identical nor inseparable. That being so, the objections on grounds of general theory cease to apply. Criticism must become more detailed.

Indeed, Prof. Soddy's theory in its present form is not a theory of variable atomic weights. Stated briefly, it may be described as the assertion that there exist a number of different substances, each having a definite and distinct atomic weight and density, which substances are inseparable by chemical means. Even if we accept the statement at its face value it is as well to emphasise that what is asserted is merely the existence of different bodies having certain identical properties. It is obvious therefore that the theory cannot be criticised merely on general principles, much in the same way as we cannot say on general principles whether or no different substances have the same density or melting-point.

The few criticisms that follow I shall confine entirely to the assertion of absolute chemical inseparability, leaving aside for the present that more tempting ground the wider ionic theory of matter. Prof. Soddy is far too dogmatic, more so than is warranted by the facts. Nor does he improve his case by the statement that "no one who has ever really tested this conclusion now doubts it, and after all they alone have a right to an opinion." It is not my intention to depreciate either the experimental ability of Prof. Soddy or the importance of the series of facts he has brought to light. But the claim that criticism of value can come neither from the general scientific public, nor even from competent chemists, is not one that can be granted to any group of investigators. The most he is entitled to state dogmatically is that when he performed certain experiments he obtained certain results, a statement which I for one am not disputing.

The facts as stated merely show that a certain series of experiments, mainly fractional crystallisation, within the limits of experimental error, has failed to alter the relative proportion of certain isotropes. Accepting the statement fully it does not warrant the conclusion. That fractional crystallisation fails to separate certain compounds may in itself mean no more than that nitrous oxide and carbon dioxide are non-separable by diffusion, or that certain mixtures of liquids are non-separable by fractional distillation. It merely proves the approximate identity of certain properties, and is not allowable to extrapolate unduly the range of properties that are identical. Needless to say I am not contending that the isotropes of lead are as different as nitrous oxide and carbon dioxide; the example is merely an illustration to show what the facts do and do not prove. Fractional crystallisation has, in practice, proved the most reliable method of separating the compounds of nearly allied elements; it does not follow that it is the most efficacious when a new problem, a new degree of similarity, has to be dealt with. The rational conclusion from the facts is that the resemblances and differences between isotropes is a problem that requires fuller and more thorough investigation.

After the test case of ionium and thorium, few, I think, will doubt that isotropes are a real discovery. That more than one element could occupy what, on current theory, appeared to be a single place in the Periodic Table has long been familiar in the iron, palladium, and platinum groups. In these cases the elements showed a surprising dissimilarity of properties. In the lead and thorium isotropes we are faced with an equally surprising similarity. The discovery therefore calls for a variety of methods in the attempt to isolate the isotropes. It would be surprising indeed if there were no differential mass action (I am using this term in a sense somewhat different from the ordinary) in chemical processes, and if the distinction between chemical and physical processes were as absolute as Prof. Soddy appears to think. Moreover, the somewhat uncertain character of spectroscopic evidence calls for caution before large inferences are based thereon. Instances when infinitesimal quantities show strong spectroscopic effects, and, on the other hand, when considerable quantities show none at all, are too well known for it to be possible to say outright whether a known spectrum refers to one element or to more than one.

These few criticisms imply no depreciation of the value of the discovery so admirably expounded by Prof. Soddy. But for the special circumstances in which the idea first came to my notice they would probably not have been written at all. There does, however, appear to me to be a certain theoretic interest in showing that the theory of variable atomic weights is untenable, and that Prof. Soddy's theory cannot be classified under this heading. There is also a very practical interest in pointing out that the next step is the careful study of the isotropes with a view to separating them, a step that should be taken without any strong preconceived idea regarding an absolute separation between chemical and physical properties. I purposely leave these conclusions in this vague general form, and have not overloaded the paper with specific suggestions concerning practical methods of separation in order not to distract attention from the paragraphs that follow.

So far I have been dealing with subjects concerning which Prof. Soddy is specially competent to speak. The subject of geologic time, however, is one which I can claim to have made my own. On this subject my criticisms of Prof. Soddy's remarks will consist in the main of the re-emphasis of conclusions the full reasons for which have been given in work previously published. Some of them may be of service to Prof. Soddy in that they will attach a greater relative importance to his estimates of the life-periods of radio active elements compared with those which some geologists think reasonable.

On no subject is it easier to publish a learned dissertation on some phase, or, now Boltwood has shown the way, to do a few more experiments on lead ratios, and thereupon assume the role of an expert and make "estimates" of geologic time of little greater value than those of previous generations. Lord Kelvin's three famous methods all in agreement should be a warning to rash successors of smaller ability and knowledge. I must, therefore, first strongly dissent from Prof. Soddy's statement that "the conclusion that lead was the ultimate product of the uranium series—has been the means, in the hands of skilful investigators, of ascertaining geologic ages with a degree of precision not hitherto possible." This statement conveys a very false impression if it is not entirely erroneous. It is not correct to state that geologic ages have been "ascertained" at all. There have been a few wild guesses, that is all. With regard to every method except that of lead ratios and pleochroic halos I have pointed this out so often and so thoroughly that further argument is superfluous. There has been no reply, and, so far as I am aware, no attempt to reply. And a very few words will suffice to show that the radioactive method, though undoubtedly a step in advance, cannot as yet be said to have "ascertained" any geologic ages whatever.

The first reason will appear to Prof. Soddy. He has been the means of showing that this method has been so uncertain as to seem to render very improbable the now established conclusion that an isotrope of lead is the end product of the thorium series. Let us take his own example of an average thorianite containing, say, 70 per cent of ThO$_2$ to 30 per cent U$_3$O$_8$. The amount of lead to be expected is about double that arising from the uranium. Analysis of thorium minerals failed to show its presence. The method is so inexact as, in this instance, to make an error of 100 per cent. With purer thorium minerals, which are not unobtainable, the error is greater still.

I am inclined to think that this proved error is small in proportion to the real error, indeed that the method is of value only in giving us some clue to the order of the result. In support of this statement the following elementary reasons, which can be amplified, extended, and generalised by going deeper into the subject, will suffice.

The method assumes that, for vast geologic ages, the minerals analysed have remained unchanged in composition, that no material has diffused in from outside, that no material has shifted to surrounding strata, that the new elementary substance (lead) formed in the mineral has remained localised in the identical spot in which it has been formed. Although the theory of mineral formation and of the diffusion of minerals through strata is in a very rudimentary state, it is possible to say that the assumption is contrary to the entire trend of geological knowledge. Such a fixity of material, if it occurs at all, must be regarded as very exceptional. The chemical constitution of formations commonly changes in most weird and inexplicable ways. As an example, the well known phenomenon of pseudomorphs will serve us very well. Fossil forms are known, originally siliceous, now consisting of carbonate of lime. Others originally calcareous, now consist of iron pyrites. Moreover, there seems to be a general tendency for particles of like substances to segregate. The great degree of purity of minerals and the formation of flints are examples of this. This fact again gives an added improbability to the assumption that the lead formed subsequently to the mineral remains quantitatively localised where it is formed. Before making such an assumption we need very cogent evidence.

Of such evidence there is none at all. All we can say with certainty is that lead is known to be a product of uranium and that lead formed from uranium is present in uranium minerals, and that as a general rule, with many exceptions, the ratio lead to uranium increases with the geologic age of the mineral. Of quantitative permanence, absolute fixity of composition, there is no evidence whatever. The evidence as we know it agrees with our common experience of the semi-fluid nature of all solids if a sufficient time be allowed. Conditions under which it is allowable to assume absolute permanence of composition, the fixity of actual particles for hundreds of milions of years are very rare indeed, and are not found under the general conditions of the substances of which lead ratios are determined. On this ground alone the error may be not one hundred per cent but many hundred per cent. Other sources of error that may be mentioned are—(1) the impossibility of knowing what proportion of the lead in the mineral is due to the uranium contained in it and what proportion to other sources, particularly original lead occluded in the mineral; (2) errors of analysis which are particularly large when the amount of lead is less than one per cent; (3) the difficulty of knowing exactly what is the geologic age of a mineral which is not so easy to determine as is that of a stratified rock.

From these few critical notes, which by no means exhaust the sources of error, there emerge two practical conclusions. The first is that dogmatism on the subject of geologic time on the part of those who have given some attention to radioactive minerals is entirely inadmissible, that the determinations are of value only in indicating the order of the time of geologic eras, and that the particular estimates may easily be wrong by many hundred per cent. No determination can be of much greater value which does not do finally and successfully what I have done for the present day and generation, co-ordinate the arguments drawn from many lines of investigation. At present to put forward actoal figures in anything but the most tentative manner is entirely inadmissible and savours of pseudo-science. The second conclusion is that those who like Prof. Soddy are investigating the properties of radioactive elements need not at present, in their estimate of the life periods of the various disintegration products, take serious account of apparently contradictory conclusions drawn from considerations of geologic time. The life periods determined by chemical means may or may not be accurate, but they are as yet the only estimates of any practical value.

Notes.

1. The question of the origin of the lead in a radioactive mineral now stands somewhat as follows:—In thorium minerals containing any considerable percentage of uranium the atomic weight gives hardly any evidence what part of the lead is original and what part is of radioactive origin. In uranium minerals containing no thorium, assuming that the quantities of radium B and Radium D are negligible, the atomic weight should be

206. Practically this atomic weight is never obtained and seldom approached, and the difference apparently points to the presence of original lead of doubtful origin and atomic weight, and therefore not readily allowed for. The necessary allowance has never been attempted, at least so far as I am aware. In a considerable number of results the proportion of lead is too small to allow the atomic weight to be determined at all. There is thus here a very large error, although smaller than those previously mentioned. Also, should it be possible to be sure of the origin of the lead, which it is not, all we could be sure of is that there is a certain percentage of uranium lead. Even then there is no certainty what proportion of this lead originates from the uranium of the mineral during the period since the mineral was laid down.

2. An early and very interesting theory of variable atomic weights is that of Sir William Crookes (Address to the Chemical Society, 1888), bearing specially on the rare elements. It will be noticed that Sir William Crookes, unlike others holding similar theories, rightly and logically postulates a concomitant variation of properties. Concerning that address many, I think, are of opinion that the last word has not yet been said on the place of the rare elements in the Periodic Table.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

Part II.—Liquids.

By IRVING LANGMUIR

(Continued from p. 256).

Oil Films on Water.

When a very small quantity of an oil, such as olive oil, is placed upon a large clean surface of water, the oil spreads rapidly upon the water surface until a definite area has been covered, and then the oil shows little or no tendency to spread further. The writer's attention was first called to this remarkable phonomenon by reading an article by A. Marcelin (*Ann. Phys.*, 1914, i., 19) on the "Minimum Thickness of Oil Films on Water."

Miss A. Pockels (*Nature*, 1891, xliii., 437) showed that very small amounts of oil on the surface of water have no appreciable effect on the surface tension, but that the surface tension begins to *decrease suddenly* when the amount of oil per unit area is increased beyond a certain sharp limit.

Lord Rayleigh (*Phil. Mag.*, 1899, xlviii., 331) repeated these experiments, and clearly pointed out the importance of the phenomena, in the explanation of the mechanism of surface tension. In Miss Pockel's and in Rayleigh's experiments a very small amount of oil is placed on water contained in a long narrow trough. The oil is prevented from spreading over the whole surface by barriers consisting of strips of glass placed across the tray and resting on the edges. By sliding these barriers along the tray the area of water, on which the given quantity of oil may spread, can be varied at will. Rayleigh measured the surface tension of the contaminated water between the barriers by Wilhelmy's method; that is, a thin blade was mounted in a balance, its plane being vertical and its lower horizontal edge dipping under the surface of the water. As the "thickness" of the oil film was varied by shifting the position of one of the barriers, the surface tension changed in the manner shown in Fig. 1 (this curve is obtained from the data of Rayleigh as recalculated to absolute units by Freundlich, "Kapillarchemie," 1909, p. 279), which represents a curve obtained with a film of castor-oil.

Thus castor-oil only *begins* to have an appreciable effect on the surface tension of water when it is present in sufficient quantity to form a layer $1{\cdot}3 \times 10^{-7}$ cm. thick. When however the thickness of the film is increased beyond this point (S in Fig. 1), then the surface tension rapidly falls as is shown by the portion of the Curve ST. From this point on, the surface tension changes only slowly (Curve TV). Rayleigh attributes the slight decrease between T and TV to a "want of homogeneity" in the oil, that is, to the presence of impurities. He says, "It would seem as if the surface still retained an affinity for some minor ingredient capable of being extracted, though satiated as regards the principal ingredient."

With olive oil Rayleigh found the thickness at which the tension begins to fall is $1{\cdot}0 \times 10^{-7}$ cm.

"Now this is only a moderate multiple of the supposed diameter of a gaseous molecule, and perhaps scarcely exceeds at all the diameter to be attributed to a molecule of oil. It is obvious therefore that the present phenomena lie entirely outside the scope of a theory such as Laplace's in which matter is regarded as continuous, and that an explanation requires a direct consideration of molecules.

"If we begin by supposing the number of molecules of oil upon a water surface to be small enough, not only will every molecule be able to approach the water as closely as it desires, but any repulsion between molecules will have exhausted itself. Under these conditions there is nothing to oppose the contraction of the surface—the tension is the same as that of pure water."

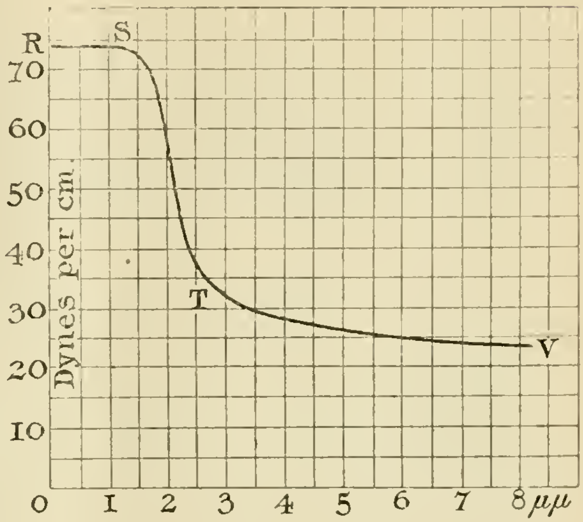

Fig. 1.

If the molecules "behave like smooth rigid spheres of gaseous theory, no forces will be called into play until they are closely packed. According to this view the tension would remain constant up to the point where a double layer commences to form. It would then suddenly change, to remain constant at the new value until the second layer is complete. The actual course of the curve of tension deviates somewhat widely from the above description, but perhaps not more than could be explained by heterogeneity of the oil whereby some molecules would mount more easily than others, or by reference to the molecular motions which cannot be entirely ignored. If we accept this view as substantially true we conclude that the first drop in tension corresponds to a complete layer one molecule thick, and that the diameter of a molecule of oil is about $1{\cdot}0 \times 10^{-7}$ cm."

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* From the *Journal of the American Chemical Society* xxxix., No. 9.

Rayleigh thus believes that the point S (Fig. 1) corresponds to a layer one molecule deep, and implies that the point T corresponds to a double layer of molecules.

Henri Devaux (Devaux has published a large number of papers between 1903 and 1914; a review of his work up to 1913 was published in the annual report of the Smithsonian Inst., 1913, p. 261; subsequent papers are *Soc. Franc. Phys.*, 1914, lv, 3, and *Ibid.*, 1914, lvii., 3) has extended this work and has developed experimental methods for the study of oil films, which are beautiful in their simplicity and remarkable in the clearness with with they demonstrate the existence of monomolecular oil films.

A photographic tray (Fig. 2) is half filled with water and a little clean powdered talc is dusted (through a piece of cloth) on to the surface. By blowing gently upon the surface the talc, together with all accidental contamination, is blown to the further end of the tray. A strip of paper A, is then placed upon the surface of the water and held by the thumbs against opposite sides of the tray. By pushing along this barrier all the oily contamination is forced into the position C (Fig. 2), while the surface below A is a perfectly clean surface of water.

This clean surface is now lightly dusted with talc. A fine wire is dipped in the oil and any visible drop hanging to it is removed. The end of the wire is then touched to be centre of the talc-covered water surface. Immediately he talc is pushed back from wire, forming a circular area f apparently clean water. If only a small amount of il is applied this circle grows only to a limited size. If oil is similarly applied to another part of the talced surface another circle will be formed without causing distortion of the first, unless the two circles come in contact. This proves that the surface tension of the oil covered water within the circles is the same as that of the clean talc covered surface.

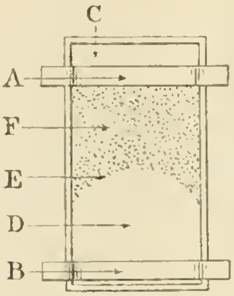

Fig. 2.

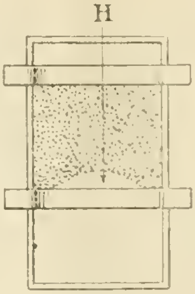

Fig. 3.

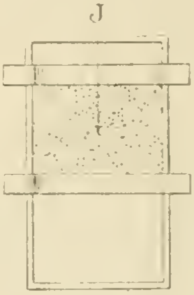

Fig. 4.

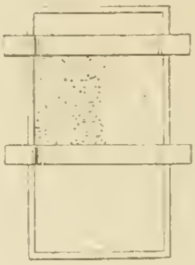

Fig. 5

Another experiment is still more instructive. Let us clean the surface as before and then sprinkle talc upon it. By blowing gently upon the water *all* the talc is readily pushed up against the barrier A. Now apply a very small amount of oi and then dust the oil contaminated surface with talc. By then blowing upon the water at the point D (Fig. 2) the talc moves back to the position E, but no further. The clear area about D is evidently clean water, while the talc-covered area F is covered by an oil film. The oil film thus covers a perfectly definite area without having any effect on the surface tension. To measure this area accurately it is only necessary to straighten the lower edge of the area F by means of the paper strip B. To accomplish this, blow continuously upon the surface (at D) while the strip B is advanced to the position shown in Fig. 3. Upon moving the barrier further the clear area H suddenly disappears, as shown in Fig. 4. If the strip is moved still further the oil film behaves like an elastic stretched membrane, and can be compressed or expanded at will. But if the lower barrier is pulled back below the position shown in Fig. 4 then the oil-covered surface ceases to expand and no longer follows the motion of the barrier.

This whole behaviour is very similar to what we should expect if we had a tray with the bottom half covered by shot. By a movable partition all the shot can be pushed to one end or the other, but in any case they cover a definite area on the bottom of the tray. If we imagine the shot to be somewhat compressible and the tray to be subjected to vibrations of small amplitude (thermal agitation of molecules), so that some of the shot can more easily mount up on the others, then we seem to have a complete analogy to the phenomena described above.

Devaux has determined the areas covered by monomolecular films from weighed amounts of oils. To do this he prepares a dilute solution (1:1000) of the oil in pure benzene and places one or two drops of this solution upon the surface of the water. The benzene evaporates and leaves the oil. Knowing the volume of the oil added in this manner and the area covered by it, the thickness of the film is readily calculated. Devaux considers that this thickness represents the diameter of the molecule. In the case of triolein, he finds this thickness to be $1{\cdot}1 \times 10^{-7}$ cm. From Perrin's value for the Avogadro's constant and from the molecular weight and density of triolein, he calculates that the theoretical value for the diameter of a molecule of triolein should be $1{\cdot}13 \times 10^{-7}$ cm.

This result, considered together with whole behaviour of the thin films, affords very conclusive proofs that these films are really one molecule deep.

Devaux has studied films of solid substances by dissolving these in benzene. He finds that these also form monomolecular films, and even in this condition exhibit the properties of solids. That is, the films possess a transverse rigidity, which disappears as soon as the amount of substance per unit area is less than that corresponding to the monomolecular film. From this fact Devaux derives "This general conclusion: the characteristic mechanical properties corresponding to certain states of a body, the surface tension of a liquid or the rigidity of a solid, persist almost intact down to molecular thicknesses, disappearing abruptly the minute we go further."

The work of Rayleigh and Devaux has not attracted the attention which it deserves. The above conclusion of Devaux's, so well supported, in some cases, at least, by experimental facts, is not at all in accord with the commonly accepted theories of surface tension, but it is exactly in line with the theories of adsorption, catalytic action, &c., which have been outlined in Part I. of this paper.

Marcelin (*loc. cit.*) describes some interesting experiments with films of oleic acid. A monomolecular film made visible by talc was produced in the manner indicated by Figs. 2, 3, and 4. Then a drop of oleic acid of considerable size was placed on one side of the oil covered surface (Fig. 4). Immediately the drop of acid spread out, pushing back the talced surface, as indicated in Fig. 5

to about one half its original area. Marcelin reasoned that the monomolecular film had been changed to one two molecules thick. He generalised this conclusion and claimed that with all oils a layer one molecule thick had no effect on the surface tension of water, while a layer two molecules thick could remain in equilibrium with a large globule of oil. This conclusion was also in accord with the observations of Rayleigh.

Devaux, in replying to Marcelin's paper, claimed that the ratio between the two areas (Fig. 5) was never as great as 1 : 2. For oleic acid he found 1 : 1·8, and for other oils, values of about 1 : 1·3. He therefore concluded that these thicker films were not two molecules thick, but were monomolecular films with closer packing of the molecules.

Labrouste (*Compt. Rend.*, 1914, clviii., 627) obtained monomolecular films of palmitic and stearic acids, and of myristin, laurin, stearin, palmitin, benzoin, cetyl alcohol, &c. Sulphur and triphenylmethane could not be made to form monomolecular layers.

Cause of the Spreading of Oils on Water.

To make further progress in the study of oil films it is important to know what is the cause of the spreading of the oil upon the water. The problem is very greatly simplified by the knowledge that the films formed are one molecule thick.

It is natural to assume that the force which causes the spreading is due to an attraction between the group molecules of the oil and those of the water. From the chemical viewpoint developed in Part I. of this paper we should not regard this attraction as emanating from the molecule as a whole, but rather from certain atoms in the molecule. This would follow directly from our conclusion that the range of forces between atoms or molecules is of the order of $0·6 \times 10^{-8}$ cm. Furthermore, it is evident that any attraction of the water for oil molecules *as a whole* would manifest itself as a solubility of the oil in the water. If, on the other hand, we can assume that a *portion* of the oil molecule is attracted to the water, while the remainder is more attracted to other oil molecules than to the water, then we have a ready explanation of the spreading on the water.

Let us consider oleic acid as an example. There is no doubt but that the carboxyl group has a marked affinity for water. The solubility of the organic acids in water, as compared with the insolubility of the corresponding hydrocarbons, is a clear indication of this fact. This affinity is due to the strong secondary valence characteristic of oxygen compounds. On the other hand, hydrocarbons have a greater affinity for each other than for water, since they are usually miscible with each other in nearly all proportions, although they are insoluble in water.

Therefore, when oleic acid is placed on water, it is probable that the carboxyl groups *do actually dissolve* in water; that is, they combine with the water chemically (by secondary valence). The long hydrocarbon chains have too much attraction for each other, however, and too little for water, to be drawn into solution merely because of the affinity of the carboxyl for the water.

As a matter of fact, by the spreading of the oil on the surface as a monomolecular layer, the carboxyl group can combine with all the water it requires, without causing the hydrocarbon chains to separate from one another.

The spreading of an oil upon water is thus due to the presence of an "active group" in the molecule; that is, some group which has a marked affinity (secondary valence) for water. This leads directly to the prediction that an oil without active groups, such as pure paraffin oil, should not spread at all. Experiment shows that this is actually the case. Hardy (*Proc. Roy. Soc.*, 1912, lxxxvi. A, 610) has studied the spreading of many oils upon water and found that pure saturated hydrocarbons do not spread; neither do such substances as benzene, cymene, &c. In attempting to explain this fact Hardy says, "The great chemical stability of the paraffins makes chemical interaction with water impossible. Some degree of chemical action would seem to be necessary to make one fluid spread as a film between two others (air and water)." He does not, however, go further than this in explaining the mechanism of the spreading. Hardy believes that the oil films are usually many molecules thick.

According to our theory of the spreading of oil films the group molecules of oleic acid arrange themselves upon the surface, so that each carboxyl group is in contact with and is combined with water, while the hydrocarbon tails are packed in side by side, and vertically placed above the carboxyl layer. The upper surface of the oil film thus consists of CH_3 groups. It is, therefore, evident that there should be no particular tendency for another layer of oil molecules to spread out on top of the first to form a second layer. In fact, since this upper surface consists exclusively of CH_3 (or C_2H_5) groups, while in a globule of oleic acid, carboxyl groups are distributed through the mass, it is natural that the oil should prefer to remain as globules rather than spread out as a layer two molecules deep. In the mass of liquid the carboxyl groups probably tend to gather into clusters, because of the greater affinity of these groups for each other than for the hydrocarbon chains. This tendency to form minute clusters explains many of the phenomena observed by Devaux in connection with his study of films thicker than monomolecular.

Now Marcelin claims that oil films in equilibrium with globules of oil consists of double layers of molecules—a result inconsistent with the above theory. The best example that Marcelin finds in support of his theory is oleic acid. The molecule of this substance contains, besides the hydrocarbon chain, two distinguishing factors—the carboxyl group and the double bond. The marked difference between the freezing points and other properties of oleic and stearic acids, suggests that the double bond may play an important role in the spreading of oils on water.

In general, from the data available, it seems that the presence of a double bond increases the solubility of a compound in water. Thus ethylene and propylene are several times more soluble in water than ethane and propane. Crotonyl alcohol, C_4H_7OH, is soluble in about six parts of water, while butyl alcohol, C_4H_9OH, requires twelve. Hexanyl alcohol is given as "very soluble," while hexyl alcohol is "slightly soluble."

This suggests that the double bond as well as the carboxyl groups may be drawn down on to the surface of the water, if there is only a limited amount of oil on a large surface of water. When a globule of oil is placed on a limited surface, however, the carboxyl groups displace the double bonds. Thus the film is one molecule deep, but in the first case the molecules are partly reclining on the surface, while in the second they are packed tightly side by side and are more or less erect upon the surface.

Fortunately, the experiments with oil films furnish means for testing this theory. Rayleigh, Devaux and Marcelin determined the thickness of oil films and assumed this to be the same as the diameter of the molecule of oil. From the present theory we are led to believe that molecules of oil on water are oriented and packed in the surface layer so that they cannot, even approximately, be regarded as spherical. We can, however, calculate the area covered by each molecule as easily as we can calculate the thickness of the film. This area is equivalent to the average cross section of the molecule in a plane parallel to the surface of the water. The thickness of the film is equivalent to the length of the molecule in a direction perpendicular to the surface.

If the square root of this cross-section differs materially from the thickness of the film we have direct evidence that the molecules are not spherical.

(To be continued).

THE NOMENCLATURE AND CLASSIFICATION OF THE NATIVE ELEMENT MINERALS.*

By EDGAR T. WHERRY.

(Concluded from p. 252)

Notes on the Table.

The first column includes the names of the species and varieties worked out according to the principles above outlined and recommended for adoption. The composition of each species and variety is given in the second column, isomorphous replacement being represented by a comma, and the element present in largest amount in each case being placed first.

Column 3 contains reasons for the names or arrangements adopted, synonyms (in quotations), and references for the minerals not listed by Dana in either the "System of Mineralogy" (1892) or the three Appendices (1899, 1909, 1915).

Native Element Minerals.

(The Chemical Elements occurring in Nature in the Free State).

Non-metals (including "semi-metals")		Combined for simplicity.
Diamond group. Isometric		New; includes all non-metals and semi-metals with isometric crystallisation, arranged in order of the Periodic system.
Diamond (isometric carbon)	C	The retention of the arbitrary name diamond is an exception to the rule for naming polymorphs, but is justified by usage.
Massive	C	"Bort."
Black massive	C	"Carbonado."
Phosphorus, isometric	P	"Yellow phosphorus," "β phosphorus." Meteoritic; very doubtful.
Arsenic, isometric	As	"Yellow arsenic." Occurrence in nature reported by Vernadskii, "Opuit Opisatel'noi Mineralogii" (Descriptive Mineralogie), i., 1908; *Centr. Min. Geol.*, 1912, 762). (Not in Dana).
Tantalum, columbiferous	Ta, Cb	
Graphite group. Hexagonal-trigonal		New; a combination of graphite with Dana's tellurium-arsenic group, arranged in order of the Periodic system.
Graphite (trigonal carbon)	C	Name retained for the same reason as that of diamond; "Cliftonite" is a meteoritic paramorph of graphite after diamond.
Arsenic, trigonal	As	
Antimoniferous	As, Sb	"Allemontite" (Dana, No. 9). Classed as a species by Dana, but there is no evidence that it is anything but a variety of arsenic containing a variable amount of isomorphous antimony.
Antimony	Sb	
Arseniferous	Sb, As	
Bismuth	Bi	
Tellurium, trigonal	Te	
Seleniferous	Te, Se	"Selentellurium" (Dana No. 6). Classed as a species by Dana, but there is no evidence that it is anything but a variety of tellurium containing a variable amount of isomorphous selenium. This selenium is present in a trigonal form which has not yet been discovered to exist independently in nature, but has been produced artificially.
Orthorhombic sulfur group		The "Sulphur group" of Dana.
Sulfur, orthorhombic	S	The spelling of this name with *f* instead of *ph* is justified by history and usage, and has been adopted by the American Chemical Society.
Seleniferous	S, Se	"Selensulphur" (Dana, No. 4), "Volcanite." Classed as a species by Dana, but there is no definite evidence that it is anything but a variety of sulfur containing a variable amount of isomorphous selenium; this selenium is present in an orthorhombic form as yet unknown independently.
Telluriferous	S, Te	"Tellursulphur."
Monoclinic sulfur group		New; includes all non-metals and semi-metals with monoclinic crystallisation.
Sulfur, monoclinic	S	"β-Sulfur," "γ-sulfur." β-Sulphur is common around volcanos, but is preservable only as a paramorph of orthorhombic sulfur; γ-sulfur has been reported to occur in nature by Vernadskii ("Opuit Opisatel'noi Mineralogii," i., 1908; *Centr. Min. Geol.*, 1912, 761); and still another form in stable crystals has been described by Suzuki (*Beitr. Min. Japan*, 1915, v., 231). (Not in Dana).

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* From the *Journal of the Washington Academy of Sciences*, vii, No. 14.

NATIVE ELEMENT MINERALS (*continued*).

Selenium, monoclinic	Se	"α-Selenium."
Arsenic, monoclinic	As	"Arsenolamprite." Crystallisation not certain.
Colloidal group. Amorphous		New; includes all non-metals and semi-metals occurring in the amorphous state.
Carbon, amorphous	C	The colouring matter of black sediments.
Silicon, dispersoidal	Si	Suggested to be the cause of the colour of smoky quartz, though without statement of evidence, by Königsberger and Müller (*Centr. Min. Geol.*, 1906, 73, Note). (Not in Dana).
Phosphorus, amorphous	P	Occurrence in nature reported by Vernadskii ("Opuit Opisatel'noi Mineralogii," 1908, i.; *Centr. Min. Geol.*, 1912, 762). (Not in Dana).
Sulfur, amorphous	S	"Sulfurite." A precipitate in sulfur spring water; also a volcanic product. (Not in Dana).
Selenium, amorphous	Se	Occurrence in nature pointed out by Zambonini ."Mineralogia Vesuviana," 1910, p. 24). (Not in Dana).
Iodine, amorphous	I	Occurrence in nature reported by Skey in 1877; Vernadskii (*Centr. Min. Geol.*, 1912, 762). (Not in Dana).
METALS		Includes the native elements of predominantly basic character.
Copper group. Isometric		When the minerals of Dana's "gold group" are arranged according to the Periodic system, copper comes first and the group is here named after it.
Copper	Cu	Wire copper, a variety, is probably a paramorph of crystalline copper after amorphous copper which has been forced through small openings while soft, corresponding to wire silver. (See below).
Argentiferous	Cu, Ag	
Mercuriferous	Cu, Hg	Brush (*Am. Journ. Sci.*, 1861, [2], xxxi., 354) throws doubt on the occurrence of this variety.
Ferriferous	Cu, Fe	
Silver	Ag	Wire silver, a common variety, is a paramorph of crystalline silver after amorphous silver which has been forced through small openings while soft (Mügge, *Neues Jahrb. Min. Geol.*, 1913, ii., 1).
Cupriferous	Ag, Cu	
Auriferous	Ag, Au	"Küstelite."
Mercuriferous	Ag, Hg	"Amalgam," in part; "arquerite," "bordosite," "kongsbergite"; included, along with argentiferous mercury, in the species "amalgam" by Dana, but there is no definite evidence that it is anything but a variety of silver containing variable amounts of isomorphous mercury.
Gold	Au	Wire gold, a variety, is probably a paramorph of crystalline gold after amorphous gold which has been forced through small openings while soft, corresponding to wire silver. (See above).
Cupriferous	Au, Cu	
Argentiferous	Au, Ag	"Electrum." Given a special name by the ancients, though recognised by them to be only an argentiferous variety of gold.
Mercuriferous	Au, Hg	Occurrence in nature reported by Schmitz (*Z. Deut. Geol. Ges.*, 1852, iv., 137). (Not in Dana).
Rhodiferous	Au, Rh	"Rhodite."
Palladiferous	Au, Pd	"Porpezite."
Iridiferous	Au, Ir	Occurrence in nature reported by Wöhler, 1834; Vernadskii (*Centr. Min. Geol.*, 1912, 760); confirmed by Chernik (*Trav. Mus. Akad., Sci. Petrograd*, 1912, vi., 49. (Not in Dana).
Platiniferous	Au, Pt	Occurrence in nature discovered by Chernik (*Trav. Mus. Acad. Sci. Petrograd*, 1912, vi., 49). (Not in Dana).
Mercury	Hg	"Quicksilver." Liquid at ordinary temperatures, but crystallises at −39° C.
Argentiferous	Hg, Ag	"Amalgam" in part. Included, along with mercuriferous silver, in the species "Amalgam" by Dana, but there is no definite evidence that it is anything but a variety of mercury containing variable amounts of silver, either in solid (isomorphous) form or (dissolved) liquid form.
Auriferous	Hg, Au	"Gold amalgam" in part. The gold is either in solid (isomorphous) form or (dissolved) liquid form.
Lead	Pb	
Iron group. Isometric		When the minerals of Dana's "platinum-iron group" are arranged according to the Periodic system, iron comes first, and the group is here named after it.

NATIVE ELEMENT MINERALS (*continued*).

Iron	Fe ..	"Ferrite." Native iron, both meteoric and terrestrial, may contain isomorphous copper, vanadium, chromium, manganese, cobalt, nickel, ruthenium, palladium, iridium, platinum, and perhaps other metals; but only two of these occur in sufficient amount to be regarded as giving rise to definite varieties.
Nickeliferous	Fe, Ni	"Edmondsonite." "kamacite," "lamprite," "plessite," "taenite." Meteoritic; the varieties are chiefly separated on the basis of structure.
Platiniferous	Fe, Pt	Occurrence in nature reported by Osann (*Ann. Phys. Chem.*, 1827, xiv., 329). (Not in Dana).
Nickel, ferriferous	Ni, Fe	"Awaruite," "josephinite," "octibbehite," "souesite." Both meteoritic and terrestrial; the minerals referred to by the synonyms have been regarded as separate species, but there is no definite evidence that they are anything but varieties of nickel containing small variable amounts of isomorphous iron.
Palladium, platiniferous ..	Pd, Pt	"Native palladium." May also contain small amounts of isomorphous iridium.
Iridium, platiniferous	Ir, Pt	"Native iridium." Named "Iridium" by Dana and others, although analyses cited show the presence of at least 19 per cent of isomorphous platinum and smaller amounts of other metals, especially copper and palladium; pure iridium is not known to occur in nature.
Platinum, ferriferous	Pt, Fe	"Native platinum." Named platinum by Dana and others, although analyses show the presenee of considerable amounts of isomorphous copper, gold, iron, nickel, rhodium, palladium, osmium, and iridium; only two of these, iron and iridium, occur in sufficient amount to be regarded as giving rise to definite varieties.
Iridiferous	Pt, Ir	Included by Dana partly under "Iridium" and partly under "Platinum."
Trigonal palladium group ..	.. ..	New; includes zinc. Classed by Dana as a semi-metal, and the trigonal minerals of the platinum-iron group.
Zinc..	Zn ..	Occurrence in nature doubtful.
Palladium, trigonal	Pd ..	"Allopalladium." May contain isomorphous silver, gold, and platinum, although none of these occur in sufficient amounts to be regarded as giving rise to definite varieties.
Osmium, iridiferous	Os, Ir	"Dark iridosmine," "sisserskite." Included, along with the following mineral, in the species "Iridosmine" by Dana; but there is no definite evidence that it is anything but a variety of trigonal osmium containing variable amounts of iridium and perhaps other metals.
Iridium, osmiferous	Ir, Os	"Light iridosmine," "nevyanskite." Included, along with the preceding variety, in the species "Iridosmine" by Dana; but there is no definite evidence that it is anything but a variety of trigonal iridium; may contain isomorphous copper, iron, ruthenium, rhodium, palladium, osmium, and platinum; of these only osmium occurs in sufficient amount to be regarded as giving rise to a definite variety.
Tin group. Tetragonal ..	.. ..	New; included by Dana in the gold group, but here separated on the basis of different crystallisation.
Tin	Sn ..	Occurrence in nature never proved beyond doubt, although there is a specimen in the U.S. National Museum from placers in California which has every appearance of being a natural product.
Colloidal group. Amorphous	.. ..	New; includes all metals occurring in the amorphous state.
Silver, amorphous..	Ag ..	Known to early German miners, but its character was first recognised by Cornu (*Zeit. Chem. Ind. Kolloide*, 1909, iv., 187). (Not in Dana).
Gold, amorphous	Au ..	Occurrence in nature reported by Cornu (*Zeit. Chem. Ind. Kolloide*, 1909, iv., 187). (Not in Dana).
Sodium, dispersoidal	Na ..	First suggested by Elster and Geitel to be the cause of colour of blue halite (*Ann. Phys. Chem.*, 1897, lxii., 559); this has been confirmed by ultramicroscopic study and by successful synthetic experiments, as shown especially by Goldstein (*Nature*, 1914, xciv., 494). (Not in Dana).
Potassium, dispersoidal ..	K ..	Suggested to be the cause of the colour of blue sylvite, by analogy with the preceding substance, by Cornu (*Centr. Min. Geol.*, 1907, 168); this has been confirmed as in the preceding instance. (Not in Dana).
Calcium, dispersoidal	Ca ..	Suggested to be the cause of the colour of certain fluorites by Doelter (*Sitzungsb. Akad. Wiss. Wien*, 1908, 1312). (Not in Dana).

COMMITTEE ON THE NEGLECT OF SCIENCE.

Members of Committee:—Sir Ray Lankester, K.C.B., F.R.S. (Chairman); the Right Hon. Lord Rayleigh, O.M., F.R.S.; Sir Hugh Bell, Bart.; Prof. G. C. Bourne, F.R.S.; Sir Bryan Donkin, M.D.; Mr. M. D. Hill; Prof. E. B. Poulton, F.R.S.; Dr. A. E. Shipley, F.R.S.; Prof. H. H. Turner, F.R.S.; Mr. A. S. E. Ackermann (Hon. Treasurer); Prof. R. A. Gregory (Hon. Secretary, 17, Grosvenor Road, Westminster, S.W. 1.

November, 1917.

In the Report of the Committee issued in July last, reference was made to the Committee appointed by H.M. Treasury to consider and report upon the scheme of examination for Class I. of the Civil Service. The Committee on the Neglect of Science, in a Memorandum submitted to the Civil Service Committee, recommended that there should be two examinations—one a qualifying examination to be taken by all candidates, and the other a competitive examination. This division is accepted by the Civil Service Committee, but no subjects are made compulsory, so that no necessity is put upon the Headmasters of the great Public Schools to give any more attention to science than has hitherto been the case. The subjoined article by Sir Ray Lankester explains the present position, and shows the opportunity that has been lost by the Civil Service Committee in bringing about a much-needed reform.

The Scheme of Examination for Class I. of the Civil Service.

At the great Conference held on May 3, 1916, in the rooms of the Linnean Society, with Lord Rayleigh, O.M., Chancellor of the University of Cambridge and late President of the Royal Society, in the Chair, to consider the "Neglect of Science" by the legislative and administrative authorities of this country and by the people generally, the following resolutions were passed unanimously:—

1. That in the opinion of this meeting it is a matter of urgency, in order to promote national efficiency in the near future, that the natural sciences should should be made an integral part of the educational course in all the great schools of this country, and should form part of the entrance examination of the Universities of Oxford and Cambridge as well as of the newer universities.
2. That it is in the highest degree desirable that the Government should exercise the large power which it possesses of encouraging the study of the natural sciences and thereby increasing the efficiency of our public servants (i.) by assigning capital importance to the natural sciences in the competitive examinations for the Home and Indian Civil Service; (ii.) by requiring some knowledge of the natural sciences from all candidates for admission to Sandhurst.
3. That this meeting is of the opinion that the method indicated in Resolution 2 is the only one by which it is practicable to bring about the desired change in the attitude of the schools and colleges throughout the country towards the natural sciences, and to make some knowledge and understanding of those sciences general. As the results of such changes will only develop in the course of years, it is urgent that the matter should be at once taken in hand by His Majesty's Government.
4. That the Committee are authorised to take such steps as they may consider appropriate in order to bring these views to the notice of His Majesty's Government.

The resolutions were moved and spoken to by a number of distinguished men, including Sir Edward Schäfer, F.R.S., Dr. Robert Bridges, the Poet-Laureate, the Right Hon. F. Huth Jackson, Lord Montagu of Beaulieu, the Master of University College, Oxford, the Earl of Portsmouth, Mr. H. G. Wells, Sir Harry Johnston, Prof. E. B. Poulton, F.R.S., of Oxford, Prof. H. H. Turner, F.R.S., of Oxford, the Rector of Exeter College, Oxford, the Master of Christ's College, Cambridge, the Right Hon. Arthur Dyke-Acland, Sir Hugh Bell, and Sir Phipson Beale. Letters and signatures in support of the general purposes of the meeting were received from a very large body of sympathisers, including representatives of such diverse interests as the President of the Royal Society, the Dean of Christchurch, Sir Guy Granet, the Hon. Charles Parsons, the Duke of Bedford, and the Lord Chief Justice of England. (See "Report of the Proceedings of the Conference on the Neglect of Science," published by Harrison and Sons, St. Martin's Lane, price 6d.).

The Committee on the Neglect of Science proceeded to take steps to bring the views of the Conference before H.M. Government, and had interviews with Lord Crewe, and with the Civil Service Commissioner (Mr. Stanley Leathes). The definite practical purpose with which they were charged was to obtain such an alteration in the examinations for first-class appointments in the Home and Indian Civil Service as would lead to an increased attention to the study of the natural sciences in our public schools and universities, whence candidates for these posts are chiefly drawn, and so to influence the tendency of all education in the country. The Government thereupon appointed a Committee to report on Science in the Educational System of Great Britain under the chairmanship of Sir J. J. Thomson, the President of the Royal Society, and also a Committee to consider and report upon the scheme of examination for Class I. of the Civil Service under the chairmanship of Mr. Stanley Leathes, C.B., First Civil Service Commissioner. The Committee on the Neglect of Science may justly be congratulated on having taken an effective part in inducing the Government to appoint these important committees. Sir J. J. Thomson's Committee on Science in the Educational System of Great Britain forwarded to Mr. Stanley Leathes's Committee the following resolution:—

> The Committee have had under their consideration certain proposals for remodelling the Competitive Examination for admission to Class I. of the Civil Service at home and in India, and in the Colonies. They are unanimous in thinking that it is indispensable that a course in Science extending over several years shall have formed a serious part of every candidate's previous education. They are, however, not prepared to trespass on the province the Committee which is dealing in detail with this Examination. They feel strongly that if the men with high scientific qualifications, who will undoubtedly be needed in the Service to a greater or less extent, are to be secured at a comparatively early age by this Examination, then candidates offering Science only (without mathematics) should in future be placed on complete equality with other candidates, and that this is not the case at present. But they recognise that there may be advantages in obtaining also by other methods scientific advisers for the Service at a greater age and with practical professional education.

The Report of Mr. Stanley Leathes's Committee is now published, and is a very weighty and valuable document, which, after giving a careful history of the Civil Service Examinations and their latest modifications, makes important recommendations of changes in the scheme of those examinations, the main object of which is stated to be to give a fair place in those examinations to the Natural Sciences, also to English and to modern languages and history. The Report is characterised by a spirit of fair dealing with the various subjects in which candidates are invited to compete, and constitutes a great advance in the direction desired by the Committee on the Neglect of Science, advocated by the speakers at the Conference of May 3, 1916. There is every reason to hope that the recommendations of the Report will at once be brought into practical operation. The Civil Service Commissioner, Mr. Stanley Leathes, is to be congratulated on a Report which will effect important improvements long desired by him, independently of the suggestions and arguments brought forward by outsiders who have endeavoured to give him support.

In a letter addressed to the Lords of the Treasury in July, 1916, the Civil Service Commissioner wrote:—

> The eminent men who have combined to bring to the notice of the Government and the country the "Neglect of Science" have laid great emphasis on this highest Civil Service Examination. They are of opinion that the revision of the scheme should be considered forthwith, and have urged their views on the Commissioners by two informal deputations. The Commissioners themselves are of opinion [*and this statement renders the recognition subsequently given to the Natural Sciences all the more significant*] that such subjects as language, literature, and history are, on the whole and for the most part of young men, the best preparation for the Higher Civil Service. But, without committing themselves to any specific line of reform, they consider that the representations of this Committee require attention, and they concur in the view that reform should be considered at once in order that the young men who go up or return to the universities after the war and desire to work for the Home Civil Service should start at once with a knowledge of the new conditions.

The result of the deliberations of Mr. Stanley Leathes's Committee thereupon appointed is the recommendation of the division of the examination into two sections—Section A *to be taken by all candidates*, and Section B optional subjects. Eight hundred marks are assigned to Section A, the creation of which is an absolutely new and important departure. The subjects are:—(1) Essay. (2) English. (3) Questions on contemporary subjects—social, economical, and political. (4) Questions on general principles, methods, and applications of Science. (5) Translation from one of the following languages not taken in Section B, viz.—French, German, Spanish, Italian, Portuguese, Dutch, Norwegian, Swedish, Danish, Russian; Latin being also an option for those who take two modern languages in B.

The optional subjects are fifty-two in number, and are marked some 100, some 200, some 400. But a candidate is allowed to take only so many, and such subjects as will make a possible total of 1000 marks, thus bringing the possible total for both sections up to 1800 marks. Ancient and modern languages—Latin, Greek, French, German, Spanish, Russian, and English—receive each 200 marks, and the history and literature of the same nationalities each 200. There are to be papers giving each 200 or 100 marks in various branches of modern history, economics, politics, law, and philosophy. Mathematics receives 400 for the lower and 400 for the higher. A candidate may try for his possible 1000 by selection from the above list, or he may take five branches of natural science—*e.g.*, lower or higher chemistry or both, lower or higher physics or both, lower or higher botany or both, lower or higher zoology or both, lower or higher physiology or both, or antropology or geography; or, again, he may take fewer natural science subjects, and fill up from the other list with subjects such as philosophy, logic, and pyschology, or French language and history. It is clear that the Committee's Report puts the natural sciences on a really fair footing in the competition as compared with classics or any literary study, though obviously the fair working of the new scheme depends upon the action of the examiners who have it in their power to make it easy or difficult to score marks in any given subject. It is noteworthy that the standard aimed at in the higher division of a science subject is stated to be that which is required when it is made the main subject of an Honours degree at the Universities; while the standard for the lower division is that required in a subject subsidiary to the main subject.

The Report does not propose to continue the holding of examinations in practical laboratory work in any of the science subjects. Experience, the Committee say, has proved them to be unsatisfactory. Some science teachers will be shocked by this omission; but, as a matter of fact, it is not difficult to set questions requiring written answers, which will clearly show whether the candidate has a real practical knowledge of his subject.

It is not possible to give in a brief space all the details of this Report. It must be read and pondered at leisure. Here we may cite a few of the more cogent remarks which it contains detached from their context. We read:—

> Public opinion demands that such coveted appointments as those of Class. I. should be made impartially without regard to class or connections or any kind of influence. . . . We want, as entrants to the Higher Civil Service, vigorous, sound, well-educated men of good intelligence. . . . The faith in competitive examination is not what it was twenty years ago. . . . Accepting the principle of open competitive examination, we regard the existing scheme (that now to be superseded) as designed to test the results of University education in general, and not the results of a special education preparatory to public service. . . . We consider that the best qualification for a Civil Servant is good natural capacity trained by a rational and consistent education from childhood to maturity. . . . We do not wish candidates to adapt their education to the examination; on the contrary, the examination should be adapted to the chief forms of general education. . . . We think it necessary to give in our scheme duly proportionate weight to the various sides of University education; and in particular to give due value to the results that should be expected from a good general education. . . . We can give an equal opportunity to modern studies; the schools and Universities must do the rest. . . . We think that the encouragement of scientific study at the University resulting from *equal treatment* may be at least equivalent to any diversion of talent from more suitable occupations that may result; a sense of injustice will be removed, and thus, we trust, harmony among men of learning may be promoted to the benefit of all forms of learning alike. . . . It will probably be admitted that the effects of the War in suspending University studies, breaking up traditions, and shaking preconceived ideas, render possible changes more fundamental than any Committee would have proposed in ordinary times, and that the various vested interests would have tolerated before the War. The Civil Service Commissioners inform us that they are prepared to welcome a reform more drastic than they could have accomplished by their own initiative. . . .

Referring to the new scheme of "optional subjects," the report states:—

> The Classical subjects will be valued at 800 marks; History and Mathematics at the same. Candidates in Natural Science taking one main subject up to the higher level, and one or two subsidiary subjects on the lower level, can obtain the same totals; while two modern languages studied as comprehensively as the Classics will be worth the same. . . The "indispensable" requirement of a school course in science (insisted on in the memorandum from Sir J. J. Thomson's Committee) must apply rather to the future than to the present. We cannot now correct the defective education of the pass.

The report gives full and convincing reasons for the innovations of requiring all candidates (papers set in Section A) to write an English essay, and also to compete in an "English" paper and in a *vivâ voce* examination; for the last 300 marks are assigned as against 100 allowed to each of the five papers set in this section.

The Report very rightly, we venture to say, proposes "no change in the limits of age (of candidates), which are at present not less than twenty-two nor more than twenty-four on August 1 in the year in which the competition is held."

In conclusion, it must be pointed out that the recommendations of Mr. Stanley Leathes's Committee stop short after securing "equal opportunity" for all subjects. With regard to the Natural Sciences, the Report expressly states that the Committee decline the responsibility of making education in them a necessity. The scheme gives the equal opportunity; "the schools and Universities," they say, "must do the rest." Though this is a real progress, the main purpose of the resolutions of the meeting of May 3 on the "Neglect of Science" is not accomplished. The difficulty remains as before—namely, that the schools and Universities are, to a large extent, in the hands of teachers of the Classics. This is the case in the old Universities; but in the great public schools it is the fact that the headmasters are, without exception, "classics," and that "the natural sciences" are treated with neglect, and their importance as an essential and dominant part of sound education is ignored.

The object of the Committee on the Neglect of Science was (and still remains) to obtain from the Civil Service Commissioners such a scheme of examination as would *compel* the managers of the great public schools to adopt a more intelligent scheme of education. The Commissioners are the only body in existence which can put pressure on the great schools and Universities. Very naturally—and perhaps correctly, but not courageously nor patriotically—Mr. Stanley Leathes's Committee refuses this responsibility. "Permissive legislation" is the limit of their courage. So it has been in former times in regard to measures for securing the public health, elementary education, and even national defence. But eventually legislation in these matters has taken a compulsory form; and so it must, without further delay, in regard to education. It is simply absurd to allow the great schools and the old Universities to administer great national funds so as to maintain, decade after decade, century after century, the vested interests of a schoolmaster-class, ignorant of, and therefore hostile to, the most important national interests—the education of our best sons in the knowledge of nature. Mr. Stanley Leathes's Committee, instead of rescuing Education from the professional vested interests of the classical schoolmasters, hands back the victim, after many professions of goodwill, to the tender mercies of those who are banded together to starve, torture, and discredit her, and remorselessly to maintain the domination and the pecuniary allurements of the "classical system."

E. Ray Lankester.

The Rarer Key Minerals.—This was the subject of an interesting lecture delivered by Mr. S. J. Johnstone, one of the experts of the Scientific and Technical Research Department of the Imperial Institute, London, at the London School of Economics on November 16, 1917. The minerals considered were those containing tungsten, thorium, molybdenum, platinum, tantalum, and zirconium. Adequate supplies of these minerals are essential to such trades as the manufacture of armour and high-speed tool steel, incandescent mantles, automatic cigar lighters, filaments for electric lamps, and furnace linings. The British Empire contains large supplies of most of the minerals, and makes important contributions to the world's production. Although the utilisation of these minerals was largely left to Germany before the war, considerable progress has since been made in their use in this country. It is understood that the lecture will shortly be issued in pamphlet form by the London School of Economics.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 15, 1917.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

"*New Gyroscopic Phenomenon.*" By E. E. Tournay Hinde.

"*Investigation into the Imbibition exhibited by some Shellac Derivatives.*" By A. P. Laurie and C. Ranken.

The paper deals with experiments made on the substances obtained by boiling shellac with carbonate of soda or borax. These solid substances, very similar in consistency to gutta-percha, are found to expand rapidly when placed in water. The control of the expansion by the addition of soluble salts is not the same as in the case of gelatine since, at any rate in a large number of cases, it does not seem to depend upon the nature of the salt, but simply upon the strength of the solution, the amount of expansion increasing with the diminution of the strength of the solution.

If the expansion is allowed to become complete in cold water, it is not possible to contract the mass again, but in the case of the expansion in a salt solution it is possible to get the mass to contract again by putting it into a stronger solution. Strong salt solutions are also found to precipitate the soluble portion of the shellac borax compound.

As a result of the experiments described, it is suggested that the facts can best be explained by supposing the shellac borax mass to consist of a soluble organic nucleus surrounded by elastic diaphragms through which the organic nucleus cannot pass, but the salt molecules can pass, the organic nucleus being soluble in water, but insoluble in strong solutions of salt.

"*Phenomena connected with Turbulence in the Lower Atmosphere.*" By G. I. Taylor.

In a previous paper by the author it was shown theoretically that a connection should exist between the rate at which heat is conveyed into the atmosphere by means of eddies, and the amount of retardation of the velocity of the lower layers of the atmosphere behind the gradient velocity due to the friction of the ground.

In the present paper the amount of the turbulence over Paris is calculated from temperature observations taken on the Eiffel Tower. It is shown that the amount is the same as that calculated from observations of the change in direction of the wind between the bottom and top of the Eiffel Tower due to the friction of the ground.

The daily variation in wind velocity which depends on the daily variation in turbulence is next discussed, and it is shown that the chief characteristics of the observed phenomena of daily variation are explained, both qualitatively and, so far as is possible, quantitatively, by the author's equations.

"*Relation between Barometric Pressure and the Water Level in a Well at Kew Observatory.*" By E. G. Bilham.

The water-level shows a well-marked response to changes of barometric pressure at all times of the year. Under similar conditions a given increase of pressure, δp, will depress the water-level in the well by an amount δu which is proportional to δp. The value of $\delta u/\delta p$ varies with the mean level of the water, but is always negative.

The validity of the equation $\delta u = a.\delta p$ was established betwen limits given by $dp/dt > 0{\cdot}5$ mb/hr., and the value of a was determined in the case of three groups of months representing high, intermediate, and low levels. The sensitiveness of the water-level to pressure was found to increase rapidly with the height of the water, the value of a for a height of 360 cm. above M.S.L. being four times as great as for a height of 200 cm. The change of sensitiveness appears to be entirely due to the change in the condition of the soil. The average value of a is 1·1 mm mb.

There appears to be no lag in the response of the well to changes of pressure, and under favourable conditions the most rapid fluctuations of pressure are shown on the water level trace.

PHYSICAL SOCIETY.

Ordinary Meeting, November 9, 1917.

Prof. C. V. Boys, F.R.S., President, in the Chair.

The President referred briefly to the great loss which the Society had sustained since the last meeting in the death of its Treasurer, Mr. W. Duddell, F.R.S.

Mr. R. S. Whipple, of the Cambridge Scientific Instrument Co., said he had known Mr. Duddell since 1898, in which year they had made his first oscillograph. Since then he had been in frequent contact with him, and could conceive of no one with whom it would be a greater pleasure to work. He was a craftsman of the first order himself, and took the greatest pains to assist in the manufacture of his inventions, pointing out the pitfalls and showing how they were to be overcome. Scientific instrument makers owed him him a great debt. He had had the privilege of being associated with him on the Council of the Physical Society for some years. The Annual Exhibition of apparatus owed its initiation to him, and its success was in large measure due to his energy and persuasive powers. He had also urged the separate publication of the Society's *Proceedings*, and had been of inestimable service to it in many ways. His death was a great loss to the Society and to science.

A paper "*On the Thermo-electric Properties of Fused Metals*," by Messrs. C. R. Darling and A. W. Grace, was read by the former.

In a previous paper (*Proceedings*, xxix., Part I.) the authors described experiments with bismuth, the apparatus then used only being capable of furnishing readings up to 560° C. Methods have now been devised in which the metals examined may be heated in the tube of an electric furnace, and observations made up to the temperature limit of the furnace. The metals experimented with were lead, tin, and antimony up to 1000° C., and zinc and cadmium up to temperatures approaching the boiling-point. No change in thermo-electric properties was noticed at fusion, except in the case of antimony, which, like bismuth, shows an abrupt bend in the E.M.F.-temperature curve at the melting-point, 632° C. This exceptional behaviour of antimony and bismuth is in keeping with the anomalous properties of these metals, both of which expand on solidification, and it is suggested that an allotropic change occurs at fusion in these metals.

In the case of lead which is used as the reference metal in thermo-electric diagrams, it is shown that extrapolation of lines in the diagram beyond 300° led to serious errors, and that although at low temperatures the E.M.F.-temperature curves are approximate parabolas, the departure from this shape above 300° is so marked as to render thermo-electric diagrams of little value.

Discussion.

Mr. Whipple said that this work opened up certain possibilities of commercial importance, as it appeared that information could be obtained of the thermo-electric properties which a particular alloy would have while it was still in the molten state. It would thus be possible by adding one or other of the constituents as required to obtain an alloy with any prescribed thermo-electric properties. At present the alloy had to be allowed to cool, and a wire of it drawn and tested. If it were not right, it had to be melted up again and its constitution altered, which was a troublesome method. With regard to the high boiling-point and low vapour pressure of tin, it was of interest to observe that Northrup had suggested a tin graphite thermometer for high temperatures up to about 1700° C. on the same lines as the ordinary mercury in glass thermometers. The tin expanding along the stem of the thermometer moved an index wire by which the temperature was indicated. What was the magnitude of the change in properties of the iron-constantan couple on passing the recalescence point of iron? He was very interested in this point, as he had not noticed any such change himself.

The President said it was a useful thing to have the futility of the old thermo electric diagram proved so thoroughly.

Dr. Willows suggested that a zinc-mercury amalgam would be an interesting substance to examine thermo-electrically for allotropic change points. Its resistance curve between 0° and 100° shows marked evidence of such changes.

Mr. Darling, in reply, said he had not detected the recalescence change with the iron-constantan couple probably because of the relatively large total E.M.F. of that couple. The change was easily detected, however, with the iron-tin couple, since the total E.M.F. is then only about 3 millivolts and a delicate galvanometer is used.

A paper on "*Triple Cemented Telescope Objectives*," by Mr. T. Smith and Miss A. B. Dale, was read by the latter.

The paper describes the four series of triple cemented thin telescope objectives which can be made from two kinds of glass, and determines their construction when first order spherical aberration and coma are eliminated. The second order spherical aberration and coma are then calculated, and the former found to be of the same sign for all optical glasses when the surfaces are spherical. The best standard attainable varies very little over a considerable range of glasses. Diagrams show the variations in the curvatures as the glasses are varied for refractive index and dispersion. Contrary to the general belief, it is found that the objectives with least second order aberrations (absolute values) are not those with the least curvatures for their refracting surfaces.

MISCELLANEOUS.

Royal Society.—Government Grant for Scientific Investigations.—Applications for the year 1918 must be received at the offices of the Royal Society not later than January 1 next, and must be made on printed forms to be obtained from the Clerk to the Government Grant Committee, Royal Society, Burlington House, London, W.

MEETINGS FOR THE WEEK.

Monday, Dec. 3rd.—Royal Institution, 5. (General Meeting).
— Royal Society of Arts, 4.30. (Cantor Lecture). "Progress in the Metallurgy of Copper," by Prof. H. C. H. Carpenter.
Tuesday, 4th.—Society of Chemical Industry, 8. "The Economics of Coal Production," by Prof. H. Louis.
Wednesday, 5th.—Society of Public Analysts, 5. "The Valenta Number as a Discriminative Test for Oils and Fats," by P. J. Fryer and F. E. Weston. "The Composition of Sharps and Bran," by H. E. Cox. "Notes on Porcelain," by W. T. Burgess. "Colorimetric Estimation of Iron," by E. R. Dovey.
— Royal Society of Arts, 4.30. Inaugural Trueman Wood Lecture, by Sir Dugald Clerk.
Thursday, 6th.—Chemical Society, 8. "Relation between Chemical Constitution and Physiological Action," by F. L. Pyman.
— Royal Society. "The Series of Legendre," by W. H. Young. "Discharge of Gases under High Pressures," by L. Hartshorn. "The Electrostatic Problem of a Conducting Sphere as a Spherical Cavity," by A. Russell. "The Zeros of Bessel Functions," by G. N. Watson.

THE CHEMICAL NEWS

Vol. CXVI., No. 3028.

THE IDENTIFICATION AND ESTIMATION OF ZINC IN WATER.

By ROBERT MELDRUM

It is well known that samples of water used for drinking and manufacturing purposes are very seldom examined for the presence of zinc, and when the presence of such is reported, more often than not the analyst fails to record the quantity present. This is all the more remarkable considering the extensive use of galvanised tanks, cisterns, and piping in water supply systems. This, in the author's opinion, is mainly due to the lack of a convenient, rapid, accurate, and sensitive method for the identification and estimation of the metal held in solution by such waters.

The solvent action of water on iron, copper, and lead is well understood, and the literature pertaining to the subject very extensive, due to the fact that well recognised methods are available for their recognition and estimation when present in solution to the extent of 1 to 10 parts per million. On the other hand, the same cannot be said about zinc either as regards its identification, estimation, or the action of various waters in bringing the metal into solution. One has only to refer to the standard works on water analysis and analytical literature in general to observe the general failure to describe in detail methods for the estimation of zinc in water.

The Film Test.

One of the universal methods advocated for proving the presence of zinc in water is by exposing the sample in a beaker, covered with a watch-glass, for twenty-four hours, and observing the formation of a film on the surface. The film has an oily appearance, and is quite distinct from a chalk film. As a confirmatory test the film is cleaned off with a strip of filter-paper and ignited with a drop of cobalt solution, when the green colour of zinc will appear. But no directions are given as to how the zinc is to be estimated by this method. There is no doubt that the film test is both reliable and sensitive when the zinc exists in the water as bicarbonate. The author has found that 1 part zinc in 200,000 can be discovered by this means in hard waters containing bicarbonate of lime. But where the zinc exists in other combinations than carbonate it is evident the film test fails. Cases have come under notice where the analyst has declared waters to be free from zinc when the same waters have developed a film on standing, and by other tests was known to be present. Waters containing traces of oil will on standing give a film which may be mistaken for zinc. But in these cases the film is not destroyed by acidifying the water.

Colorimetric Ammonium Sulphide Process.

The author has attempted to estimate the zinc in water by means of a colorimetric ammonium sulphide process, but it has been found that this is valueless when the zinc exists in less amount than 1 in 100,000, which apparently is the limit of the test. After numerous experiments it has been found the best and most reliable way to make the estimation is as follows:—Three graduated 100 cc. test measures or Nessler's tubes are placed on a black tray, board, or cardboard near a window or other good source of subdued daylight, the first being filled with tap-water only, the second with distilled water, and the third with sample. To No. 1, No. 2, and No. 3 is added 1 cc. strong HCl, and well mixed. To No. 2 is now added 1 cc. standard zinc solution containing 1 grm per litre of metallic zinc, and again well mixed. There is now added 2 cc. ammonium sulphide to all the tubes, and again well mixed and allowed to remain at rest for fifteen minutes. At the end of this time a distinct but faint cloudiness or opalescence will have developed in the standard tube, the presence of which will be made evident by comparison with tube No. 1 which contains no zinc. If by this time no cloudiness appears in the sample tube it may be safely inferred that no zinc is present to the extent of 1 in 100,000. If present in the sample to this amount or more, the estimation is made by adding more standard solution of zinc to the standard tube until equal opacities or cloudiness is obtained. For this purpose the standard zinc solution diluted ten times is a convenient strength to use, or containing 0·0001 grm. Zn per cc. It is more certain to view the opacity in a horizontal line of vision several feet away from the tubes at an angle of 20 to 30°. By repeatedly changing the line of sight from left to right, and at greater and less distances, differences or equality of opacity may be better observed.

Unless the above instructions are rigidly carried out in detail failure to detect and estimate the metal accurately is sure to result. The most essential point is to add sufficient acid to the sample to more than neutralise the alkaline salts present, which in the majority of cases will not require more than 1 cc. strong HCl; then, again, sufficient alkaline NH_4HS must be further added to neutralise the free acid and to leave a surplus over to combine with the zinc, which, in the majority of cases, will not require more than 2 cc. The presence of manganese, iron, lead, copper, and alumina will of course interfere seriously with the value of the process, that the zinc cannot be identified or estimated. The very fact of the sample striking a brown, dark yellow, or black colour with the NH_4HS will prove the presence of these metals, which at once will make the process inoperative. If alumina is present in the sample it will be estimated as zinc or mistaken for the latter. It so unfortunately happens that alumina is present, more or less, in the majority of waters and will be precipitated with the zinc. This process therefore is only of use when the character and mineral constituents of the sample is known.

In the presence of iron and alumina the most convenient method is to acidify 200 cc. of the water with 1 cc. strong HCl, or more if required, and evaporate to 80 cc., and add 1 cc. strong ammonia, and filter off the iron and alumina through a very small ashless filter-paper. Allow to cool, and make up to 100 cc., and add 2 cc. NH_4HS, the resulting opalescence being compared with the standard opalescence. As the precipitated F_2O_3 and Al_2O_3 carries down more or less zinc it is necessary to redissolve this in 5 cc. weak HCl, and wash with 4 to 5 cc. water, and reprecipitate, filter, and wash. The filtrate need not exceed 10 cc. if the iron and alumina is small. This may be added to bulk previous to making up to 100 cc. In many classes of water this will be found to be the only available method, or some modification of same, which offers itself for the estimation of zinc and its identification.

The following experiments will give a good indication of the capability of the colorimetric ammonium sulphide process as applied to water:—

Expt. 1.—50 cc. distilled water with 0·005 grm. Zn in solution + 2 cc. NH_4HS. No cloudiness or opalescence, but flocculent precipitate immediately forms, which settles to bottom and measures about 3 cc. Thus 5 mgrms., or 0·01 per cent, or 1 in 10,000, can easily be estimated in 50 cc. by precipitation, filtering, and weighing.

Expt. 2.—50 cc. distilled water with 0·001 Zn in solution with 2 cc. H_2S only, or 2 cc. NH_4HS, yields strong and pronounced opalescence in one minute. This equals 1 mgrm. of zinc in 50 cc., or 0·002 per cent, or 1 in 50,000.

Expt. 3.—50 cc. distilled water + 0·0005 Zn with 2 cc. H_2S only yields distinct opalescence in five minutes. This equals ½ mgrm. in 50 cc., or 0·0001 per cent, or 1 in 100,000.

Expt. 4.—100 cc. distilled water + 0.0005 Zn in solution + 1 cc. NH_4HS. No trace of opalescence or cloudiness in fifteen minutes when viewed horizontally. This test therefore fails to detect 0·0005 per cent, or 1 in 200 000.

Expt. 5.—100 cc. distilled water + 0·001 Zn + 1 cc. NH_4HS. No opalescence or cloudiness; therefore failed to detect 1 Zn in 100,000.

Expt. 6.—100 cc. distilled water + 0·002 Zn + 1 cc. NH_4HS. Very faint opalescence or cloudiness in fifteen minutes viewed horizontally. This must be compared with water only, cloudiness is so faint. Thus 1 in 50,000 barely detected by the test.

Expt. 7.—Ditto as above, but with 0·2 cc. of NH_4HS. Opalescence very weak when compared with that produced by the addition of 1 cc.

Expt. 8.—Tap water free from zinc and containing 26 $CaCO_3$ per 100,000 + 1 cc. NH_4HS only. No cloudiness or opalescence in five minutes, but remains bright and clear for that time or few minutes longer, but in ten minutes becomes quite cloudy. This is due to precipitation of the $CaCO_3$ by the ammonium carbonate formed, and proves the necessity of acidifying all waters previous to treatment with NH_4HS. For instance, 100 cc. tap water with 0·002 Zn + 1 cc. NH_4HS = 1 in 5000, yields pronounced cloudiness in ten minutes, which is twice as strong as that produced by the same quantity of Zn in distilled water. The importance of this point cannot be overlooked.

Expt. 9.—100 cc. tap water free from zinc with 1 cc. 20 per cent HCl + 1 cc. NH_4HS becomes cloudy in ten minutes. This shows that insufficient acid has been added, and shows the importance of well acidifying the water previous to addition of NH_4HS.

Expt. 10.—100 cc. tap water + 0·002 Zn + 1 cc. strong HCl, well mixed and allowed to rest for a minute + 2 cc. NH_4HS. Very pronounced opalescence in five minutes. A blank experiment made without zinc remains clear and bright with no trace of cloudiness. This equals 2 mgrms. Zn per 100 cc., or 0·002 per cent, or 1 in 50,000. The experiment also proves that this particular sample of hard water develops no cloudiness with NH_4HS.

Expt. 11.—100 cc. tap water + 0·002 Zn + 1 cc. strong HCl + 2 cc. NH_4HS. 100 cc. distilled + 0·002 Zn + 1 cc. strong HCl + 2 cc. NH_4HS. 100 cc. tap water + acid + NH_4HS only. Tap water without zinc develops no opacity in fifteen minutes, but remains quite clear and bright. The remaining two tests yield equally distinct and prononnced opacities in ten minutes. This equals 2 mgrms. per 100 cc., or 0·002 per cent, or 1 in 50,000. The above opacities are viewed horizontally or in a thickness of 2 cm.

Expt. 12.—100 cc. distilled water + 0·001 Zn + 1 cc. strong HCl + 2 cc. NH_4HS. 100 cc. tap water + 0·001 Zn + 1 cc. strong HCl + 2 cc. NH_4HS. 100 cc. tap water only. Equally distinct, but faint opacities in fifteen minutes when viewed horizontally and compared with tap water only, = 1 in 100,000, which apparently is about the limit of sensitiveness of the test. To detect smaller amounts than this by this method will of course mean evaporating 200 cc. of the sample to 100 cc., or 500 cc. to 100 cc. after acidification with HCl.

It is hardly needless to point out that all the glass vessels used must be free from zinc. But a blank experiment under the exact conditions of operation will discover if zinc is being yielded by the glass vessels or not. The same remarks apply to the alumina in the glass. These points are important if the concentration of evaporation be necessary.

Summary.

As already pointed out this colorimetric process will in the majority of cases, where the sample contains iron and alumina, also copper and lead, be the only one available to the analyst. Moreover, the test is a very convenient one in the application to all samples, as the absence or presence Fe, Cu, Pb, is at once decided. But it so happens that the majority of waters which contain zinc also contain lead and iron, but these usually seldom exceed 0·01 per 100,000, and do not seriously interfere with the direct colorimetric estimation.

A CONTRIBUTION TO THE THEORY OF SOLUTION.*

By E. J. HARTUNG, B Sc.

When two completely miscible liquids, which do not visibly react with each other, are mixed together in any proportion, the physical properties of the mixture are found, in general, to differ from those calculated according to the simple mixture law. This divergence has been ascribed to changes in a state of aggregation of the molecules of one or both liquids, to the formation of a definite compound between the two liquids, or to both these causes combined. From a qualitative standpoint the theory is quite satisfactory; on the other hand, it is extremely difficult to apply quantitatively, except in the simplest cases. The reason for this lies in our lack of satisfactory knowledge of the molecular condition of most liquids and of the changes in this condition which take place when different liquids are mixed together. Nevertheless, some fairly satisfactory quantitative results have been obtained in a few simple cases.

Dolezalek (*Zeit. Phys. Chim.*, 1908, 64) endeavours to apply a quantitative theory in the simplest possible cases—

(i.) Where both liquids are unassociated and one solvate is formed between them.

(ii.) Where one liquid is normal and the other partly associated, while no solvate is formed.

He exemplifies (i.) with mixtures of acetone and chloroform, and (ii.) with mixtures of benzene and carbon tetrachloride. By assuming that neither the solvate molecules nor the associated liquid molecules are volatile as such, he shows that a knowledge of the partial pressures of the two components in the vapour phase enables quantitative data as to the extent of solvate formation or association to be determined, and also enables the physical properties of any mixture to be calculated. The only physical properties he considers, however, are vapour pressure and density.

In a later paper, Dolezalek and Schulze (*Ibid.*, 1913, 83) make a careful study of the liquid pair ether-chloroform. This appears to furnish a simple case of two non-associated liquids combining to form a single solvate with equimolecular proportions of the parent substances. The authors show how certain physical properties of these mixtures, such as heat capacity, vapour pressure, specific volume, refractive index, and viscosity, may be calculated with fair accuracy. Additional evidence of the formation of a solvate is given by the fact that an equimolecular mixture of ether and chloroform solidifies as a single substance when cooled to a temperature about 30° above the freezing-point of pure ether.

With a view to applying the theory of Dolezalek, Hubbard (*Ibid.*, 1910, 74) has examined certain physical properties of a number of binary liquid mixtures. The discussion of his results does not seem to have yet appeared.

Denison (*Trans. Faraday Soc.*, 1912, viiii., Part I.), while recognising the formation of associated molecules of one or both liquids as a possible cause of departure from the mixture law, mainly devotes his attention to solvate formation, and attempts to show that the divergences are to be ascribed to it, that more than one solvate is not likely to be present, and that the composition of the solvate may be inferred from a quantitative study of such divergences. However, the examples chosen by him to illustrate his theory are not suitable for this purpose.

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* A Paper read before the Faraday Society.

Holmes (*Trans. Chem. Soc.*, 1906, 1774) and Holmes and Sageman (*Ibid.*, 1909, 1919) consider a number of aqueous and non-aqueous solutions from the property divergence standpoint. They reject the solvate hypothesis, and propound a purely physical theory in explanation of their results.

The work in this present paper was undertaken at the suggestion of Prof. Orme Masson, after the publication of Denison's results, in order to afford more suitable tests for his theory.

Experimental Work.

The experimental work in this paper consists of a series of measurements of the density, heat capacity, and heat change on mixing, of mixtures of selected pairs of liquids. The liquids were carefully purified as follows:—

Ethyl Ether.—This was purified in the manner recommended by Wade and Finnemore (*Ibid.*, 1909, 1842). A considerable quantity of Merck's pure ether was washed in small portions with ten successive changes of distilled water to remove alcohol. The ether was then dried over granular calcium chloride for some days, and afterwards over phosphorus pentoxide for a week. The almost anhydrous liquid was then kept in the dark over shredded sodium and sodium amalgam for several months to remove the last traces of water and also any peroxides. When required for use, portions of this stock were distilled from fresh sodium and amalgam, and kept in the dark. A density determination gave—

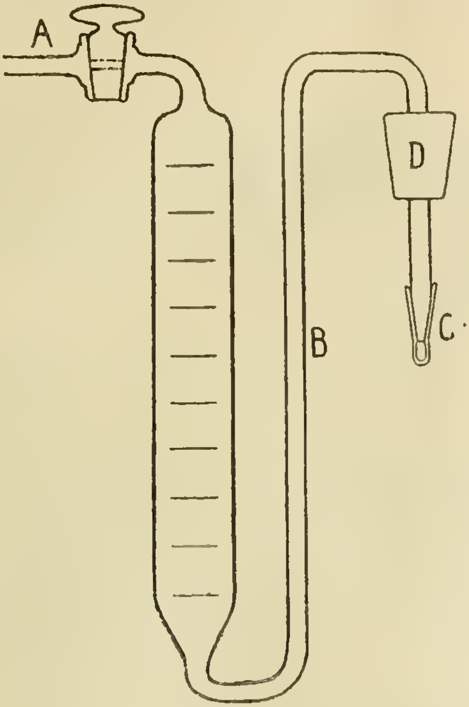


Fig. 1.

$$D_{20}/_{4} = 0{\cdot}71308$$

The density under the same conditions of the ether used by Dolezalek and Schulze (*loc. cit.*) was 0·71305.

Nitrobenzene.—This substance was made by nitrating benzene under the proper conditions, and, after separating and washing the product, fractionally distilling several times until the boiling-point was constant (209°)—

$$D_{20}/_{4} = 1{\cdot}20369.$$

Aniline.—A sample of Schuchardt's pure aniline was repeatedly fractionally distilled through an air condenser until the boiling-point was constant (184°). It was preserved in the dark until required, and was perfectly clear and colourless.

$$D_{50}/_{4} = 1{\cdot}02197. \quad D_{25}/_{4} = 1{\cdot}01744.$$

Methyl Alcohol.—A sample of Schuchardt's pure acetone-free methyl alcohol was boiled for seven hours with metallic calcium under a reflux condenser, closed with a calcium chloride tube, to remove water. It was then fractionally distilled from fresh calcium, and the fraction coming over between 65·15° and 65·24° (bar. 756 mm., cor.) was collected.

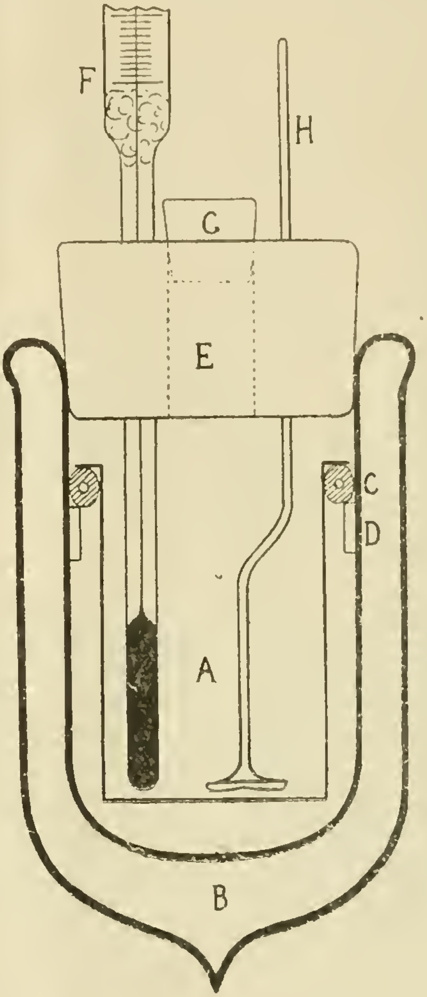


Fig. 2.

$$D_{25}/_{4} = 0{\cdot}78740.$$

Carbon Tetrachloride.—A sample of Schuchardt's pure reagent was available, but it proved to contain some considerable amount of carbon disulphide. The method of purification advocated by W. Schmitz-Dumont was used (*Chem. Zeit.*, 1897, 21). This consists in adding to the sample a saturated solution of potassium hydroxide in alcohol, and then heating to 60° for half-an-hour. If carbon disulphide is present, the liquid turns brown, and potassium xanthate is precipitated. The liquid is then washed repeatedly with water until all the alcohol is emoved. This process was carried out, and after drying over calcium chloride for some hours, the carbon tetrachloride was fractionated. The product coming over between 76·22° and 76·38° (bar. 741 mm., cor.) was collected.

$$D_{20}/_4 = 1·58469.$$

The density and heat capacity of each pure liquid were then determined at the temperature at which the series of mixtures was to be examined (20° or 25°). Each mixture of the chosen pair was accurately made up by weighing in a glass-stoppered Erlenmeyer flask, the less volatile liquid being invariably weighed first. The properties of the mixture were then studied.

Density.—This was determined in a narrow-necked density bottle of 25 cc. capacity, provided with a well-fitting glass stopper. The bottle was carefully calibrated with distilled water beforehand, and was always used with a suitable counterpoise. The measurements were made in a well-regulated water thermostat provided with a standard (Kew certificate) thermometer. The mixture was introduced into the bottle directly from the mixing flask by blowing it through a fine capillary tube. After bringing the level of the liquid in the bottle to a fixed mark on the neck, the inside of the neck above the liquid was carefully dried with narrow strips of filter-paper, and the stopper inserted prior to weighing. All density measurements refer to water at 4° as the standard.

Heat Capacity.—This was determined by a method previously described by the present author (*Trans. Faraday Soc.*, 1915, xi., Part I.). After the density of the mixture had been determined, the remainder of the liquid in the mixing vessel was introduced by gentle suction into a weight pipette of special form (Fig. 1), and from this into the calorimeter, and the heat capacity was determined. The weight pipette consisted of a cylindrical vessel of 100 cc. capacity, provided with a tap (A) and a long suitably bent delivery tube (B), close by a well-fitting ground-glass cap (C), and carrying a rubber stopper (D) to fit into the opening in the calorimeter.

Heat Change on Mixing.—This was determined by directly mixing the two liquids in known amount in a modified form of the calorimeter used for the heat capacity measurements. The calorimeter (Fig. 2) consisted of an internally silvered thin copper vessel (A) (for one series of mixtures a thin glass calorimeter was used), fixed by means of a rubber ring (C) resting on a cardboard ring (D) in the interior of a silvered Dewar tube (B), which was closed by a well-fitting rubber stopper (E). The temperature was read by a calibrated Beckmann thermometer (F). The liquids were introduced by means of the weight pipette (Fig. 1) through a hole in the stopper, ordinarily closed by a small rubber stopper (G). A thin glass stirring rod (H), terminated by a thin flat disc of glass about 1·5 cm. in diameter, ensured rapid mixing of the two liquids. This stirring rod was lubricated through the stopper with a little vaseline or phosphoric acid. The under side of the stopper (E) was heavily coated with several layers of tinfoil to protect it from the action of vapours in the calorimeter.

The method of experiment was as follows:—

The two pure liquids were introduced into weight pipettes of similar form (Fig. 1), and each carefully weighed. The Dewar tube and calorimeter had been immersed meanwhile in a water thermostat at the temperature of experiment until the reading shown by the Beckmann thermometer was constant (somewhat lower than that shown by the thermostat thermometer). This condition took some considerable time to attain, as the Dewar tube was an efficient insulator. The thermostat was provided with a perforated cardboard cover to diminish radiation. The pipette containing the more volatile liquid was then immersed in the thermostat for half-an-hour or so with the mouth of the delivery tube over the edge of the bath so that it should not get wet. The glass cap (Fig. 1, C) was then removed, and the delivery tube inserted into the calorimeter through the hole in the rubber stopper, into which its own stopper fitted. The liquid was introduced by gently blowing through a calcium chloride tube attached to the other end of the pipette. The calorimeter was then closed and the pipette weighed after again putting on its cap. The pipette containing the second liquid was then immersed in the thermostat, and after half-an-hour, when the calorimeter temperature was quite constant, the calorimeter was opened, the delivery tube of the pipette inserted as before, and the liquid blown in. The two liquids were rapidly mixed by the stirring rod and the temperature changes noted. Radiation corrections were then applied, and the second pipette weighed. The water equivalent of the calorimeter being known, the number of calories evolved or absorbed on mixing was then calculated.

(To be continued).

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

Part II.—Liquids.

By IRVING LANGMUIR.

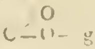
(Continued from p. 26[illegible].)

Determinations of the Shapes of Group Molecules.

In order to determine the cross-sections and lengths of molecules in oil films experiments similar to those of Marcelin were undertaken. The oil, or solid fat, was dissolved in freshly distilled benzene (usually 50 mg. in 100 cc.), and, by means of a calibrated dropping pipette, one or two drops of the solutions were placed upon a clean water surface in photographic tray. The maximum area covered by the film was measured by the method indicated in Figs. 2, 3, and 4.

Dividing this area by the number of molecules of oil on the surface, the area of water covered by each molecule is readily obtained. This must also equal the cross-section of the molecules. The results are given in the first column of Table I. The number of molecules of oil on the surface was found by first calculating the number of grm.-molecules of substance in the one or two drops of benzene solution added, and then multiplying this by N, the number of molecules per grm.-molecule, which, according to Millikan, is equal to $6·062 \times 10^{23}$.

An examination of these results shows that the cross-sections of the molecules vary over quite a wide range—from 21 to 126×10^{-16} sq. cm. The three saturated acids, palmitic, stearic, and cerotic, all occupy nearly the same areas ($21—25 \times 10^{-16}$ sq. cm.), notwithstanding the fact that the number of carbon atoms in the molecules increase from 16 to 26. Each tristearin molecule covers a space of 66×10^{-16}, which is exactly three times that of a stearic acid molecule. Furthermore, the molecule of cetyl-palmitate takes up an area of 23×10^{-16} sq. cm., which is again about the same as that of stearic acid.



Thus we see that each $\overset{O}{\overset{\|}{C}}-O-$ group occupies an area of about [illegible]3×10^{-16} sq. cm., no matter whether it occurs in an acid or in an ester. This area is substantially independent of the length of the hydrocarbon chain to which the active group is attached.

These measurements afford striking proof of the theory outlined in the preceding pages, according to which the spreading of an oil on water is caused by the presence of certain active groups in the molecule.

We may also calculate the length of the molecules in a direction perpendicular to the surface. The volume of each molecule is found by dividing the "molecular volume" of the oil (M/ρ) by the Avogadro constant N. By dividing this volume by the cross-section of each molecule the length of the molecule in a direction perpendicular to the surface can be obtained. The results are given in the third column of Table I.

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* From the *Journal of the American Chemical Society*, xxxix., No. 9.

Table I.—*Preliminary Measurements of Cross-sections and Lengths of Molecules.*

Substance and formula.	I. Cross-section Sq. cm.	II. √ Cross-section Cm.	III. Length Cm.	IV. Length per carbon atom.
Palmitic acid, $C_{15}H_{31}COOH$	21×10^{-16}	$4·6 \times 10^{-8}$	$24·0 \times 10^{-8}$	$1·5 \times 10^{-8}$
Stearic acid, $C_{17}H_{35}COOH$	22 ,,	4·7 ,,	25·0 ,,	1·39 ,,
Cerotic acid, $C_{25}H_{51}COOH$	25 ,,	5·0 ,,	31·0 ,,	1·20 ,,
Tristearin, $(C_{18}H_{35}O_2)_3C_3H_5$	66 ,,	8·1 ,,	25·0 ,,	1·32 ,,
Oleic acid, $C_{17}H_{33}COOH$	46 ,,	6·8 ,,	11·2 ,,	0·62 ,,
Triolein, $(C_{18}H_{33}O_2)_3C_3H_5$	126 ,,	11·2 ,,	13·0 ,,	0·69 ,,
Trielaidin, $(C_{18}H_{33}O_2)_3C_3H_5$	120 ,,	11·0 ,,	13·6 ,,	0·72 ,,
Cetyl palmitate, $C_{15}H_{31}COOC_{16}H$	23 ,,	4·8 ,,	41·0 ,,	2·56 ,,
Myricyl alcohol, $C_{30}H_{61}OH$	27 ,,	5·2 ,,	41·0 ,,	1·37 ,,

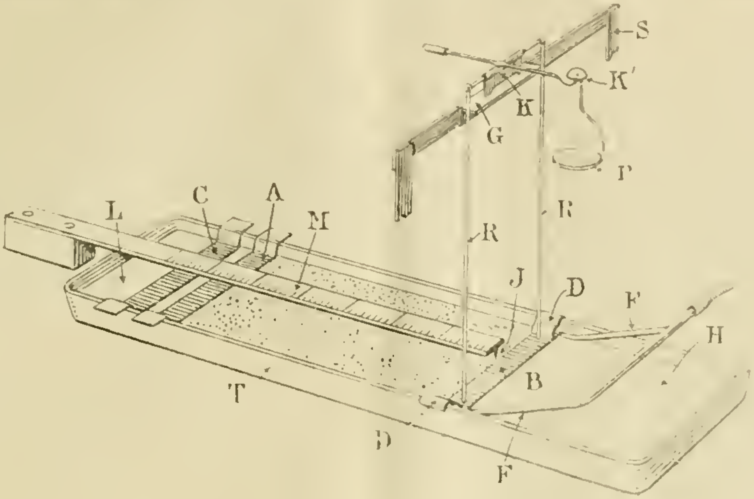


Fig. 6.

It is interesting to compare these lengths with the cross-sections. As a rough approximation we may assume that the dimensions of the molecule in directions parallel to the surface can be found by taking the square root of cross-section. This is equivalent to assuming that each molecule in the surface film occupies a volume represented by a square prism with its axis vertical. The length of the square side, which we shall refer to as the average diameter, is given in the second column of Table I., while the height of the prism (or the length of the molecule) is given in the third column.

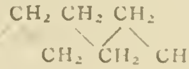
It is seen at one that the molecules are very much elongated. Thus the length of the palmitic acid molecule is about 5·2 times the average diameter. The results prove that the molecules arrange themselves on the surface with their long dimension vertical as is required by the theory.

The molecule of tristearin has the same length (perpendicular to the surface) as the stearic acid molecule, but three times the cross-section. Thus each of the three active groups has been drawn down on to the surface of the water while the hydrocarbon chains are packed in side by side and are erect upon the surface.

The case of cetyl palmitate is interesting. Here the length of the molecule is 41×10^{-8} cm., or nearly twice that of the palmitic acid molecule, while the average diameter is only $4·8 \times 10^{-8}$ cm., or about the same as the palmitic acid molecule. The molecule contains two long hydrocarbon chains connected by a carboxyl group. In palmitic acid the length of such a group is 24×10^{-8} cm. If the length of this group were nearly a constant quantity then we should have to assume that in the cetyl palmitate film the two chains in each molecule are arranged one above the other with the carboxyl in the middle. On this assumption, however, the only part of the molecule in contact with the water would be the CH_3 on the end of one of the hydrocarbon chains, so that there should be no tendency for this substance to form a monomolecular film on water. Solid paraffin for example dissolved in benzene and placed on water does not give a monomolecular film but gives a thick film (10—40 molecules thick) of variable thickness depending on the rate at which the benzene is allowed to evaporate.

The present theory therefore compels us to conclude that the carboxyl group of the cetyl palmitate is on the surface of the water and that both hydrocarbon chains are packed in side by side above the carboxyl group. The area of water covered by the carboxyl is the same as in the palmitic acid, so that the two hydrocarbon chains side by side do not have any greater cross-section than the one in the palmitic acid. But each chain is extended to nearly twice the length in the first case that it is in the second.

This result indicates that the hydrocarbon chain does not have any definite shape or arrangement of its atoms in space, but rather that the chain should be regarded as extremely flexible. Thus in the palmitic acid film the arrangement of the atoms in the chain is probably somewhat as follows:—



$$\begin{array}{ccc} CH_2 & CH_2 & CH_2 \\ & \diagdown\diagup\diagdown & \\ CH_2 & CH_2 & CH_2 \end{array}$$

while in the cetyl palmitate the chains are packed closely, so that the arrangement becomes more near that represented by the typical formula—

$$\begin{array}{ccccccccccc} & H & & H & & H & & H & & H & \\ - & C & - & C & - & C & - & C & - & C & - \\ & H & & H & & H & & H & & H & \end{array}$$

In a diamond the distance between adjacent carbon atoms is $1{\cdot}54 \times 10^{-8}$ cm., and this probably represents the minimum distance within which carbon atoms can approach. In the hydrocarbon molecule we should expect that they would be considerably further apart than this.

Dividing the length of the molecule (Table I.) by the number of carbon atoms in the chain we obtain the average *vertical distance* between adjacent carbon atoms in the chain. The results are given in the fourth column of Table I. In all cases except that of cetyl palmitate the distance is less than the distance between atoms in the diamonds. This is a clear indication that the atoms cannot be arranged linearly, but rather must be arranged along a zig-zag or curved line. The observed cross section (23×10^{-16} sq. cm.) is ample to allow the carbon atoms to be arranged in some such manner and still be separated from each other by distances greater than $1{\cdot}54 \times 10^{-8}$ cm.

The results obtained with the substances containing unsaturated hydrocarbon chains affords striking confirmation of the theory already proposed, according to which the double bond is to be regarded as an active group. Each oleic acid molecule covers a surface of 46×10^{-16} sq. cm. whereas the saturated acids only cover about half as great a surface. This same difference is manifest in triolein and triclaidin when compared with tristearin. The data given in the fourth column shows this effect even more clearly. Whereas with all the saturated molecules the average vertical distance between carbon atoms is greater than $1{\cdot}2 \times 10^{-8}$, it lies between $0{\cdot}62$ and $0{\cdot}72 \times 10^{-8}$ for the unsaturated molecules.

We thus have a proof that the film in equilibrium with a globule of oleic acid on water, which Rayleigh and Marcelin supposed to be two molecules thick, is in reality only one molecule thick. Marcelin found that the film in equilibrium with the globule was about twice as thick as that obtained with the maximum extension. Since the latter is clearly one molecule thick Marcelin concluded that the former must be two molecules thick.

From the data of Table I., however, we see that an oleic acid film, in maximum extension, is only half as thick as that of stearic acid, so that, when doubled in thickness by placing a globule of oleic acid on the surface, the film becomes of the same thickness as that of stearic acid, and the cross-sections of the molecules are also the same. There is thus no reason for assuming the existence of a layer two molecules deep.

These preliminary experiments furnish very convincing evidence of the correctness of the theory developed in the present paper.

To make further progress it became desirable to measure the forces involved in the spreading of oils, in other words to measure the changes in surface tension produced by oil or fat films. Rayleigh and Hardy had used Wilhelmy's method, but this method cannot be employed for measuring the forces exerted by solid films and even for liquid films great difficulty is caused by the glass or mica plates becoming greasy, so that the angle of contact no longer remains zero.

In carrying out measurements of the areas covered by oil films by Devaux's method one is struck by the magnitude of the forces acting on the paper strips. If the strips are not very firmly attached to the edges of the tray they may be pushed out of position when a drop of oleic acid is placed on the water. It occurred to the writer that a very satisfactory method of measuring the forces could be developed by a horizontal balance arranged to weigh the force acting on one of these paper strips.

This new method not only avoids the difficulties in connection with contact angles and solid films, but has the marked advantage that it affords a highly sensitive and accurate *differential* method of measuring slight changes in the surface tension of water.

A diagrammatic representation of the apparatus used for this purpose is given in Fig. 6. The water is placed in an enamelled tray, T, which is about 60 cm. long and 15 cm. wide. Above the tray is arranged a small balance with knife edge, K, resting on a glass plate, G, fastened to a support, S. One end of the beam of the balance has a counter weight while the other has a small knife edge, K', from which hangs a small pan, P. Two glass rods, R and R', cemented to the knife edge, extends downwards and pass though two small holes in a strip of paper, B, which floats upon the surface of the water in the tray. To prevent the paper from being softened by the water it may be prepared by dipping in a solution of paraffin in benzene.

The length of the paper strip B is about 5 mm. less than the width of the tray, so that it can move freely without touching the sides of the tray.

The surface of the water between the strips A and B is covered by an oil film by placing one or two drops of a benzene solntion of the oil on the water.

As the strip A is moved forward the oil film is pushed ahead of it until it begins to exert a force on the paper strip B. This force also tends to make the oil film flow around the ends of the strip B into the space B behind the strip. To prevent this two air jets are directed by the tubes T T' against the surface of the water between the ends of the strip B and the sides of the tray. The air blast is regulated and maintained constant by allowing a portion of the air to escape from a tube dipped to a given depth in water. Two pieces of sheet metal, D and D', are attached to the edges of the tray confining the air blast as much as possible to the surface of the water at the ends of the strip B.

(To be continued).

COMMITTEE ON THE NEGLECT OF SCIENCE.

The following is the July Report referred to in our last issue (p. 267):—

July 1917.

The Committee submits the subjoined report upon matters which have engaged its attention since the meeting held at Burlington House on May 3, 1916.

1. *Government Committee on Science.*

In June, 1916, Lord Rayleigh, Sir Ray Lankester, Dr. Shipley, Prof. Bourne, and Mr. M. D. Hill had an interview with Lord Crewe at the Privy Council Office. Lord Crewe then informed these representatives of the Committee that the Government had decided to appoint a Committee on the subject of scientific education in Secondary Schools, and he hoped that the Committee on the Neglect of Science would have the opportunity of giving evidence before it. The Committee referred to by Lord Crewe was afterwards appointed, with Sir Joseph Thomson as chairman. Its terms of reference are:—To inquire into the position occupied by Natural Science in the educational system of Great Britain, especially in Secondary Schools and Universities, and to advise what measures are needed to promote its study, regard being had to the requirements of a liberal education, to the advancement of pure science, and to the interests of the trades, industries, and professions which particularly depend on applied science.

After correspondence with the Secretary of the Government Committee, it was arranged that representatives of the Committee on the Neglect of Science would attend on October 24, 1916, to state the views of the Committee. Sir Ray Lankester was selected as the representative witness of the Committee, and Sir Bryan Donkin, Prof. H. H. Turner, and Prof. G. C. Bourne also attended to give corroborative and supplementary evidence.

The evidence submitted on behalf of the Committee consisted of (*a*) the following resolutions passed at the meeting called by the Committee on May 3, 1916;—

1. That in the opinion of this meeting it is a matter of urgency, in order to promote national efficiency in the near future, that the natural sciences should be made an integral part of the educational course in all the great schools of this country, and should form part of the entrance examination of the Universities of Oxford and Cambridge as well as of the newer Universities.
2. That it is in the highest degree desirable that the Government should exercise the large power which it possesses of encouraging the study of the natural sciences, and thereby increasing the efficiency of our public servants (i.) by assigning capital importance to the natural sciences in the competitive examinations for the Home and Indian Civil Service; (ii.) by requiring some knowledge of the natural sciences from all candidates for admission to Sandhurst.
3. That this meeting is of the opinion that the method indicated in Resolution 2 is the only one by which it is practicable to bring about the desired change in the attitude of the schools and colleges throughout the country towards the natural sciences, and to make some knowledge and understanding of these sciences general. As the results of such changes will only develop in the course of years, it is urgent that the matter should be at once taken in hand by His Majesty's Government.
4. That the Committee are authorised to take such steps as they may consider appropriate in order to bring these views to the notice of His Majesty's Government.

(*b*) A list of speakers who supported these resolutions at the meeting held on May 3, 1916, with a marked copy of the report of the Proceedings giving extracts from the speeches and from letters of approval received by the Committee.

(*c*) The Memorandum, with the list of signatories on the Neglect of Science, published in *The Times* of February 2, 1916, and contained in a marked copy of the Proceedings of the Conference.

(*d*) Copies of the complete report of the Conference on the Neglect of Science held on May 3, 1916.

(*e*) Independent evidence by Sir Ray Lankester as to the urgent need for replacing "classical education" by "education in the natural sciences and in English."

It was also suggested that the Government Committee might select from the list of speakers and supporters given in the report of the meeting called by the Committee on the Neglect of Science on May 3rd, names of men prominent in professions dependent on science, and also of those experienced in educational matters who would give evidence if requested to do so.

It was especially desired by the Committee on the Neglect of Science, that the Government Committee shall ascertain definitely from the authorities of the great Public Schools, the actual facts as to the time given in the school course, in each year, to the study of natural sciences. The figures should be given for each year—say, first year (average age 13—14), second year (average age. 14—15), third year (average age, 15—16), fourth year (average age, 17—18)), sixth year (average age, 18—19), or as nearly as possible under successive years and corresponding ages. The return should show for *each* year:—

(*a*) Number of boys of that age and year in the school.
(*b*) Number of boys of that age and year attending classes in natural science.
(*c*) Number of hours per week assigned to work in school for boys of that age and year.
(*d*) Number of hours per week assigned to natural sciences for all boys of that age and year.
(*e*) Number of hours per week assigned to classics (*i.e.*, Greek and Latin languages and history) for all boys of that age and year.
(*f*) Similar returns for mathematics, English language, and literature, French language.

A separate return should show what number of boys in each year are specially exempted from other studies and assigned to classes in natural science. The number of hours a week thus taken from other studies and assigned to natural science, in the case of these exceptional boys, should be stated.

A further return—of great importance in the present enquiry—is one showing the number of masters employed in the school in each of the main divisions of study, and the number of hours and of boys taught per hour in each of the main divisions of study (say, classics, English, French, mathematics, natural sciences).

It should further be stated whether any "form-masters" teach natural science, and, if so, how many? What are the objections to natural science being taught by a form-master?

It should also be stated whether masters who teach natural science have a less remunerative career in the school open to them than those who teach classics.

It was urged that the Government Committee could do nothing more useful than remove the stumbling-block of compulsory Greek at the Universities of Oxford and Cambridge. Though a majority of the people who have given attention to the matter is now in favour of reform, the way is blocked by the non-resident voters at Oxford and Cambridge, and it should be cleared by Government action. The conviction of the necessity of this reform is stronger than ever it was; but without external aid from the Government neither Oxford nor Cambridge can carry it out. More direct encouragement of science is also needed, so that there should be an increased number of careers open for highly trained men. This stimulus might be attained by the expansion of scientific services similar to the Royal Observatories and the National Physical Laboratory, and the establishment of other services in which men who had received the highest scientific training could find careers.

2. *The Headmastership of Eton College.*

At a meeting of the Committee in July, 1916, it was decided to send a letter to the Chairman of the Governing body of Eton College urging the importance of appointing a headmaster with scientific knowledge or sympathies in succession to Canon Lyttelton. The following letter signed by members of the Committee was sent:—

"As members of a Committee which, amongst its other duties, is pledged to use every endeavour to make the natural sciences an integral part of the educational course in all the great public schools of this country, we beg leave to request that you will, on our behalf, represent to the Governing Body of Eton College the importance of selecting from among the candidates for that office a headmaster who, if not actually a man of distinguished scientific attainments, is at least conscious of the national and educational value of the natural sciences and is resolute to introduce such reforms as will place them on a parity with other branches of study.

"If there should be among the candidates a man of recognised scientific attainments, we venture to suggest that it would be appropriate in the present crisis of our national affairs that the choice should fall upon him. It is acknowledged that, when peace is again restored, our country will be called upon to exert its best energies, not only to repair the waste of war, but also to secure its own position in the future, and to compete successfully with other nations. To attain this object it is necessary that those who guide the destinies of the country should acquire the scientific habit of mind and a knowledge of Nature so as to be able to form accurate judgments upon scientific problems. Eton College above all other schools contributes a large proportion to the leading politicians and landowners and men of local influence, and to the heads of great commercial houses. The future of the country is therefore largely in the hands of those educated there, and we respectfully submit to the Governing Body of the College that they will be studying the best interests of the

Empire by appointing a Headmaster who may be relied upon to carry out an educational policy which will ensure those placed under his charge shall not remain ignorant of the value of natural sciences nor think lightly of their influence on the prosperity of the country."

The Headmaster appointed was the Rev. C. A. Alington, Headmaster of Shrewsbury School. Mr. Alington was a scholar at Trinity College, Oxford, where he took a 1st Class Classical Mods. in 1893, and 1st Class Lit. Hum. in 1895. He is a Fellow of All Souls.

3. *Committee on Civil Service Examinations.*

The Lords Commissioners of His Majesty's Treasury appointed in November, 1916, a Committee to consider and report upon the existing scheme of examination for Class I. of the Home Civil Service. The terms of reference are:—"To submit for the consideration of the Lords Commissioners of His Majesty's Treasury a revised scheme such as they may judge to be best adapted for the selection of the type of officer required for that class of the Civil Service, and at the same time most advantageous to the higher education of this country, and, in framing such a scheme, to take into account, so far as possible, the various other purposes which the scheme in question has hitherto served, and to consult the India Office, the Foreign Office, and the Colonial Office as to their requirements in so far as they differ from those of the Home Civil Service."

The members of the Committee are as follows:—Mr. Stanley Leathes, C.B., First Civil Service Commissoner (Chairman); Sir Alfred Ewing K.C.B., F.R.S., Vice-Chancellor of the University of Edinburgh; Dr. W. H. Hadow, Principal of Armstrong College, Newcastle-upon-Tyne, and Vice-Chancellor of Durham University; Sir Henry A. Miers, F.R.S., Vice-Chancellor of the University of Manchester; Prof. W. G. Adams, Gladstone Professor of Political Theory and Institutions in the University of Oxford. The Secretary of the Committee is Mr. D. B. Mair, Civil Service Commission, Burlington Gardens, W.

On March 13, 1917, the following Memorandum was submitted to this Committee by the Committee on the Neglect of Science, together with copies of the Report of the Proceedings of the meeting held on May 3rd, 1916:—

Memorandum on the Desirability of Modifying the Civil Service Examination (Class I.).

It may be remembered that on May 3, 1916, at a conference held in the rooms of the Linnean Society, Burlington House, the resolutions quoted below were agreed to unanimously. Lord Rayleigh, O.M., F.R.S., Chancellor of the University of Cambridge, presided at the meeting, and was supported by the Master of University College, Oxford, the Rector of Exeter College, Oxford, the Master of Christ's College, Cambridge, Mr. Robert Bridges, the Poet Laureate, Sir Ray Lankester, and many others.

1. That it is in the highest degree desirable that the Government should exercise the large power which it possesses of encouraging the study of the natural sciences and thereby increasing the efficiency of our public servants (i.) by assigning capital importance to the natural sciences in the competitive examinations for the Home and Indian Civil Services; (ii.) by requiring some knowledge of natural science from all candidates for admission to Sandhurst.
2. That the Committee are authorised to take such steps as they may consider appropriate in order to bring these views to the notice of His Majesty's Government.

The Committee therefore begs to submit the following suggestions for the consideration of the Committee on the cheme of Examinations for Class I. of the Home Civil ervice, viz.:—

I. That there should be two examinations held for ndidates in Class I.—

(a) A qualifying examination in which all candidates must satisfy the examiners before being allowed to enter for.

(b) A competitive examination.

In the former (a) a candidate should be required to give evidence of a good all-round education in which natural science, modern languages and literature, and elementary mathematics, but not Latin or Greek, should also be included as necessary subjects. The Committee is of opinion that the standard required in natural science should be higher than that which will probably be considered sufficient in the General School Examination passed by most candidates at the age of 16 to 17 years.

II. If it be considered undesirable to introduce this qualifying examination, the Committee suggests, as an alternative, that candidates be admitted to the competitive examination only if they possess certificates of having passed a higher school examination of the nature indicated in Circular 849 of the Board of Education, and further can produce evidence of having received adequate instructions in natural science during the interval between passing the General School Examination and the time of their leaving school.

III. (b) *Competitive Examination.*—With regard to (b) the Committee holds that for certain appointments in the Civil Service an advanced knowledge of natural science is of paramount importance, while for others it is less necessary. Hence it suggests that certain posts should be open only to candidates who can show proficiency in certain branches of natural science. Special knowledge of law, history, or mathematics would be required for other posts, and should be made subjects of competition in the case of candidates for those posts, either with or without one or more branches of natural science.

The Committee believe that by these means well-educated men with special aptitude and ability in certain subjects would be sorted out into the positions which they are best capable of filling.

The need for revised conditions of entrance into the Civil Services, in order to ensure that administrative officers possess sufficient scientific or technical knowledge to give adequate consideration to modern problems, is felt in countries other than our own. For example, in Germany there has been for a number of years a movement for the acceptance of technically trained men into higher posts of the Civil Service, and under the stress of war the Institution of German Engineers submitted a letter upon the subject to the Chancellor of the German Empire in June, 1916. The Committee is indebted to Dr. A. J. Makower for the following translation of this letter:—

Translation of a Letter from the Institution of German Engineers to the Chancellor of the German Empire.

Berlin, June 13, 1916.

Your Excellency,—The Committee of the Institution of German Engineers urges that steps should be taken by modification of the law in the confederated States, and particularly in Prussia, by removing the obstructions of the law of 1906 concerning eligibility for the higher posts in the Civil Service, so as to make it possible that not only lawyers but also graduates of the technical high schools should be able to take up careers in the higher Civil Service.

Already before the war, after exhaustive discussions extending over many years, the demand has been expressed that candidates for the higher posts in the Civil Service should be given a scientific academic training, so as to enable them to have a full understanding of the conditions of public life, upon which industrial questions and the requirements of trade and commerce exert a preponderating influence at the present day. The War has confronted the State with an unexpected number of new problems that have caused it to call into its service the intellect of the most diverse professions. This extension of admission to the higher careers in the Civil Service that has been introduced under the pressure of the circumstances of the time must be extended, the barriers that still exist in this respect must be removed, if it is to be possible to ensure the full development of the economic forces of the country after the war.

It has now become an imperative necessity that the demand that has been expressed for many years by the Institution of German Engineers should be fulfilled, and that University graduates, particularly of the Technical High Schools, should be admitted to the higher grades of the Civil Service, so as to place the selection for this career on a broader basis.

Already ten years ago, on the occasion of the discussions in the Prussian Diet on the Government proposals concerning the change of the course of study for law (1903) and later, after their rejection, in the discussions of the law concerning eligibility for careers in the higher Civil Service (1906), the Government admitted readily that the training of the higher Civil Service officials did not correspond with the requirements of the day. The removal of this defect was unsuccessfully attempted at that time by a proposed reform of the academic curriculum, and is supposed now to have been achieved by means of the law of 1906 by measures that only take effect subsequent to the academic study. Later experience has shown that the method that has been adopted is hardly likely to be able to impart to the coming generation of State officials a special understanding of the economic processes that govern our life in days.

The training of the majority of higher-grade officials in the Civil Service and Communal bodies that has become customary and has been determined by the law, consists in a secondary school education that has a particular bias towards the humanities, and a short University course which is almost exclusively composed of legal subjects. *The course of study laid down for the lawyers is at the same time and without change also the course of study for the officials of the Civil Service.*

This rigid connection of professions, that must be admitted to be very different in their practice, is unique in the whole educational system of Germany. It constitutes an inherent contradition, and has gradually become an unsurmountable obstacle, which will in all probability wreck the system that was to be built on the foundation of the law of 1906.

The system of training that has been described above has created the peculiar situation that all young people who have a leaning towards any one of the numerous branches of the Civil Service, whether by family tradition, ideals, or special capacity, are forced, even against their inclination for science, to devote themselves completely to a legal training in order to pass the first law examination, as this provides practically the first documentary evidence obtainable for admission to a Civil Service career in the Empire, the States, the Communities, and many other posts. This route is closed to the graduates of other faculties for instance, of all the experimental sciences—by the provisions of the above-mentioned Prussian law and of similar laws in the other German States, as well as by the custom that is developing in consequence of this law of appointing lawyers for administrative work.

In consequence of the preponderating influence that technical questions and the requirements of industry have to-day on all branches of public life and the increasing participation of the provinces, communities, and towns in technical and scientific enterprises, civil servants are called upon to deal with problems, the expert solution of which calls for just the type of mental equipment that is provided by the Technical High Schools. The greater part of the education at these institutes is not based on retrospection and definition, but is directed forwards and designed with a view to productive activity. An education among such surroundings must give at least as good a training for a Civil Service career as an education the principal aim of which is to classify the particular requirements of life according to legal conceptions. The knowledge of law and administration that is required by civil servants can be acquired to-day in every Technical High School.

A large number of eminent men have been produced by a training in science, industry, and economics. These men, with broad views and organising capacity, have been in the past, and are still at the present moment, successful leaders in private industrial enterprises. The forcible exclusion of the intellect that is available amongst these circles from participation in the higher Civil Service constitutes a waste of the intellectual powers of our nation. The monopoly that has been wrongly accorded to the legal course of study must be removed and admission to a career in the higher Civil Service must be made free to graduates of the Technical High Schools.

(Signed) The Committee of the "Institution of German Engineers."
Directors { Rieppel and Taaks.
D. Meyer and G. Linde.

(To be continued).

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, November 22, 1917.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows :—

"*Bactericidal Properties Conferred on the Blood by Intravenous Injections of Diamino-acridine sulphate.*" By C. H. Browning and R. Sulbransen.

1. Whereas antiseptic compounds are in general greatly reduced in their bactericidal activity by the presence of serum it has been found that salts of 3.6-diamino-acridine, both unsubstituted and also various derivations with methyl-groups substituted in the amino-side-chains, or in the benzol-rings, or in both situations, are enhanced in their lethal action on bacteria by the presence of serum; this is also the case with the salt of 3.6-diamino-10-methyl acridinium. Thus, in the presence of serum these acridine derivatives constitute the most powerful bactericidal agents known for pathogenic organisms such as *Staphylococcus aureus* and *B. coli*. Their action is slowly progressive, and concentrations which at first merely inhibit proliferation of bacteria ultimately prove lethal. In addition, salts of diamino-acridine and diamino-methyl acridinium (sulphate and chloride respectively) are relatively non-toxic for mammalian tissues and devoid of harmful effects on phagocytosis; hence they have been recommended for use in the local treatment of infected wounds and other accessible infective lesions.

2. Of these substances the sulphate of 3.6-diamino acridine has been found specially suitable for intravenous injection on account of its low toxicity. It has also much less agglutinating action on red blood corpuscles than diamino-methyl-acridinium chloride.

3. By means of an intravenous injection of diamino acridine sulphate in a dose which had no harmful effect on the treated animal (rabbit), it has been possible to confer antiseptic properties on the blood, so that the serum from a specimen of blood withdrawn as late as from two to two-and-a-half hours after the treatment failed to yield a culture when inoculated with *Staphylococcus aureus* or *B. coli*. Serum obtained from the animals before treatment yielded abundant growth of both organisms when similarly inoculated. So far as we know, these are the first observations in which it has been recorded that bactericidal properties for these organisms have been con-

ferred on the blood serum *in vivo* by the administration of non-lethal doses of a substance of defined chemical constitution.

4. These acridine compounds are also excreted in the urine and the bile. Indications are thus afforded for investigations with a view to chemo-therapeutic interference in septicæmic conditions and in infections of the kidneys and bile passages.

"*The Pelmatoporinæ: An Essay on the Evolution of a Group of Cretaceous Polyzoa.*" By W. D. Lang.

The evolution of this sub-family is considered in detail. In order to present the facts intelligibly they are marshalled according to the following theoretical considerations:—

1. The species lie along diverging lineages; towards the bases or proximal ends of these are forms (radicals) with less calcareous skeletal matter and less elaboration of structure, and these forms appeared earlier in geological time; towards their higher or distal ends are forms with more skeletal matter and more elaborate structure, appearing later in geological time.

2. The evolutionary tendency was to deposit the increasing superfluity of calcium carbonate where it least interfered with the organism's bionomics; if possible in such position and shape as might even be useful to the organism. Sooner or later the race perished through being unable to cope with its constitutional and increasing habit of excessive secretion of calcium carbonate.

3. There is a predisposition in radical forms of different lineages to deposit their superfluous calcium carbonate along corresponding tracts, and with it to build up similar secondary structures. They differ in comparative rate of building and in amount of elaboration, as well as in details of architecture and ornament. Consequently, (*a*) in most cases it is possible to predict the general history of a lineage from an examination of one of its early terms; and (*b*) lineages often present series of homœomorphic forms; while characters diagnostic of genera, and still more of congeneric lineages, often appear trivial and of little importance to the organism.

4. The "Law of Recapitulation" holds good in post-embryonic growth-stages, not only of the individual but of the colony as expressed by the individual constituents at successive distances from its starting point. In fossil polyzoa, astogeny (as Cumings called the development of the colony) is more easily observed than ontogeny.

5. Periodicity is displayed by the Pelmatoporinæ in their evolution.

The relations of the various forms are inferred from their adult morphology. Their stratigraphical distribution is considered in order to confirm these relations, though the evidence of stratigraphy can only be negative; it can contradict a supposed relation, but cannot affirm it. Finally, astogeny of forms is used to test morphological results.

Incidentally, results obtained by W. K. Spencer in his investigations on evolution of cretaceous star-fishes are compared and found generally to correspond with results described in this paper.

SOCIETY OF GLASS TECHNOLOGY.

Ordinary Meeting, November 21, 1917.

Mr. Duncan Webb in the Chair.

The following paper was read:—

"*Gas Firing and the Glass Industry.*" By J. W. Cobb, B.Sc., F.I.C.

In manufacture, coal forms the basis of all fuels used, and the applications of gaseous fuels obtained from coal marks a distinct advance upon direct firing. In the old types of furnace, where the fuel is burnt close to its work, the heat available is only a small percentage of the whole, due to the fact that the fall in temperature of the flame from entry to exit is only small. There is great danger, too, in the light ash which is formed, being carried forward to exercise its baneful effects as a flux on furnace linings, &c., and also its decolorising effects on any glass it may come in contact with. The waste heat from direct fired furnaces may be utilised, say, for steam raising, but only in a makeshift manner. Attempts, too, have been made to utilise this waste heat to pre-heat the air required for combustion, but owing to difficulties of furnace design these attempts are far from from being successful. A fact often lost sight of in heating air by passing it through hot flues, is that air is transparent to radiant heat, and is only affected by actual contact with the hot walls of the flue. Thus preheating by passing air through hot flues of a large cross section is very ineffective.

A great step in furnace work was the introduction of the Siemens regenerative furnace. The action of this and other producers depends upon simple chemical and thermal principles. Coal is burnt away from the furnace proper with the formation of carbon monoxide. This latter gas, then, is delivered into the furnace together with air, and burning there to carbon dioxide produces the heat required. In addition, the waste hot gases leaving the furnaces are made to pass through chambers filled with chequered brick-work, to which they yield their heat. By suitable means the ingoing air and gas is afterwards passed through this hot brick-work, and so is heated before entering the furnace, resulting in an enormously increased temperature of combustion. In addition the regenerative chambers serve as filters for the dust or ash in the gases.

The Siemens producer was then described in detail, a series of lantern diagrams illustrating various points being shown. In the Siemens producer the depth of fuel is large and there is considerable frictional resistance to movement of gas. Thus the rate of production is slow with ordinary draught. If the rate has to be increased air must be blown in, and this has its drawbacks. With a natural draught Siemens the heat evolved in the producer is small and easily dissipates. With forced draughts this heat is much larger, and so the temperature rises to such an extent as to cause clinkering. In order to keep down the temperature near the fire bars steam is blown in. The advantage secured by this is not confined to clinker prevention. The steam, acting on the red hot carbon forms a mixture of carbon monoxide and hydrogen (water gas), and this mixture is very valuable fuel in itself. Its production, too, is accompanied by an absorption of heat from the layer of hot coal near the fire bars. Thus the blowing in of steam not only cools the producer and prevents clinkering, but it adds carbon monoxide and hydrogen to the producer gas without dragging in nitrogen; *i.e.*, the percentage of combustible gas is raised and the temperature realised finally is increased. It must be recognised that there are limits to the amount of steam that can be blown in. Any excess results in the formation of carbon dioxide, or may even pass on into the furnace chamber unaltered, where it has the harmful effects of an inert gas. The best proportions of air and steam have to be determined by practice. At this point several modern gas producers were described and illustrated by lantern diagrams. Special details were given of the Taylor producer, the Kerpely producer, and of producers of the Mond type. The production of ammonia, low temperature regeneration, and the washing of producer gas by the Mond system was also discussed in detail.

The remainder of the paper dealt with the problem of recuperation, the heating of small furnaces, the use of town's gas, and the necessity of securing, if possible, gas of fairly constant composition.

In the discussion which followed, Messrs. Duncan Webb, Connolly, and Simpson took part, and Prof. Cobb replied.

The next meeting of the Society will be held on December 19 in the University, Sheffield.

NOTICES OF BOOKS.

A Short Account of Explosives. By ARTHUR MARSHALL, A.C.G.I., F.I.C., F.C.S. London: J. and A. Churchill, 1917. Pp. viii+96. Price 5s. net.

THE large number of people who are nowadays interested in the manufacture and use of explosives will find that this book provides them with very interesting information, giving a clear account of the various explosives which have come into use in recent years, and describing accurately the processes involved in making them. The characteristic properties of military and commercial high explosives are fully discussed, and a very interesting account is given of methods of ignition and detonation. Although the information given is necessarily brief and put as far as possible in non-technical language, the reader will find that he can get from the book a very clear idea of the nature of the common explosives and their uses in different circumstances.

The Preservation of Wood. By A. J. WALLIS-TAYLER, A.M.I.C.E. London: William Rider and Son, Ltd. Pp. xix+372. Price 10s. 6d. net.

OWING to the growing scarcity of timber and the shortage of labour it is becoming increasingly necessary to make the most of all stocks of wood, and if possible to lengthen the life of articles made of timber by paying special attention to methods of preservation. The appearance of this book is therefore distinctly opportune, and all buyers and users of timber will find that it will well repay careful study. Methods of destroying dry rot and fungi generally and drying by artificial means are fully discussed, and accounts are given of the various preservatives employed, with special attention to the pressure system of treatment which is described at great length with many illustrations and diagrams. The chapter on fire-proofing, giving the results of various processes, is particularly interesting. The question of the cost of treating wood is discussed at some length, and statistics are given as to the life of preserved woods and the absorption of preservatives.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Bulletin de la Société Chimique de France.
Vol. xxi.-xxii., No. 8, 1917.

Method of Separation of Stereoisomeric α-Halogen Ethylenic Acids (Stable and Labile).—J. Bougault.—In the preparation of α-halogen acids from the ethylenic acids it often happens that both stereoismers (stable and labile) are simultaneously obtained. These isomers have different solubilities in neutral solvents, but it is often very difficult to separate them by these solvents, and is successful in the case of the less soluble derivative. The iodine compounds, moreover, readily oxidise in neutral solvents, setting free iodine, and as the crystallisations always take a fairly long time an appreciable alteration is thus caused. The author has successfully separated these halogen acids by the following method:—The aqueous solution of the potassium salts of the α-halogen ethylenic acids are slightly acidified with acetic acid, when the acid salt of the stable halogen acid, $(R.CH=CX.CO_2)_2KH$, is precipitated almost integrally, the only necessary condition being that the free acid itself should be insoluble in water. The small quantity of stable acid remaining in solution can be eliminated by shaking with ether. The isomers which have been thus separated are α-iodo, α-bromo, and α-chloro cinnamic acids, and α-iodo and α-bromophenylcrotonic acids.

MISCELLANEOUS.

Life of Sir William Ramsay.—Sir William Tilden has just completed and placed in the hands of Messrs. Macmillan and Co. for publication his Life of Sir William Ramsay, the famous chemist.

Royal Institution.—A General Meeting of the members was held on the 3rd inst.; Sir James Crichton-Browne, F.R.S., Treasurer, in the chair. The Chairman announced that the Managers, at their meeting held this day, had appointed Dr. Arthur Keith, M.D., F.R.S., Fullerian Professor of Physiology. Dr. Arthur Keith is Conservator of Museum at the Royal College of Surgeons, and author of "The Human Body," "The Antiquity of Man," and other well-known works. W. B. Faraday, Mrs. Spencer Gollan, Albert Gray, Mrs. Albert Gray, Burnett Tabrum, Mrs. Williamson, and Frederick Chamberlain were elected members.

British-Barimar Thermit Welding Co.—To prevent any misunderstanding we would point out that the British-Barimar Thermit Welding Co. mentioned in our issue of November 23 must in no way be confused with Thermit, Limited, 675, Commercial Road, London, E. 14, who are the owners of the Alumino-Thermic Process Patents, and in no way connected with the new company referred to, who merely hold a license to work certain of the Patents belonging to Thermit, Limited. Thermit, Limited, were originally established in 1904, and about eighteen months ago the whole of the shares were sold to the Birmingham Metal and Munitions Co., Ltd., Birmingham. Thermit, Limited, continue their manufacture of various thermit compounds, and are at present especially engaged upon the manufacture of certain metals and alloys in connection with munitions of war, and repairs to heavy castings, &c.

Testing and Standardisation of Motor Fuel.—On October 16 a paper was read by Mr. E. Lawson Lomax, M.Sc., F.C.S., before the Institution of Petroleum Technologists on the testing and standardisation of motor fuel, in which the subject was discussed in a thoroughly practical spirit. The Redwood and Engler methods of distillation were carefully compared, and it was pointed out that the former is much the quicker and easier to perform. The new process suggested is as convenient as the Redwood process, and gives results which agree very well with those obtained by the Engler method. Special apparatus is necessary, and may be obtained from Messrs. A. Gallenkamp and Co. The determination of sulphur was also discussed in the paper and the estimation of olefines, and the author's suggestions as to the need of standardising motor fuel deserve careful consideration.

MEETINGS FOR THE WEEK.

MONDAY, 10th.—Royal Society of Arts, 4.30. (Cantor Lecture). "Progress in the Metallurgy of Copper," by Prof. H. C. H. Carpenter.

WEDNESDAY, 12th.—Royal Society of Arts, 4.30. "Technical Training for Disabled Soldiers and Sailors," by Lord Charnwood.

— Faraday Society, 7.30. (Annual General Meeting). "Study of the Refractivities of Saturated and Unsaturated Compounds," by Gervaise le Bas. "Thermal Properties of Sulphuric Acid and Oleum," by A. W. Porter. "On Iso-piestic Solutions," by W. R. Bousfield.

THURSDAY, 13th. Royal Society of Arts, 4.30. "The Trade of India with Russia, France, and Italy," by D. T. Chadwick.

— Royal Society. "The Formation of Nitrites from Nitrates in Aqueous Solution by the Action of Sunlight and the Assimilation of the Nitrites by Green Leaves in Sunlight," by B. Moore. "The Transition from Rostro-carinate Flint Implements to the Tongue-shaped Implements of River-terrace Gravels," by J. R. Moir.

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THE CHEMICAL NEWS

VOL. CXVI., No. 3029

NITROGEN, CHLORINE, AND SULPHATES IN RAIN AND SNOW.

By E. LYLE PECK.

FROM October 20, 1916, to June 8, 1917, we continued the investigation made by Artis (CHEMICAL NEWS, cxiii., 3), investigating forty-one samples. There were thirty-three precipitations of rain and eight of snow, or 15·86 inches of rain and 22 inches of snow, equivalent to 17·69 inches of rain.

The heaviest rainfall (2 inches) occurred March 13 and May 23; the largest amount of snow (4 inches) fell on January 12 and 21, and again on April 7. The largest amount of sulphates was found during the months of November and March, with an average of not quite 20. Of the various substances determined the chlorine was the most constant—7·1 parts per million in twenty determinations.

We considered 12 inches of snow equivalent to 1 inch of rain, and 226,875 lbs. as the weight of 1 inch of rain upon an acre.

We desire to express our thanks to Dr. N. Knight for suggestions in carrying on this work.

Cornell College, August 5, 1917.

TABLE I.—*Parts per Million.*

Date.		Amount (inches).	Rain or snow.	Direction.	Sulphate.	Nitrate.	Nitrite.	Nitrogen in free NH_3.	Nitrogen in alb. NH_3.	Chlorine.
October..	20	½	R	W	12 36	0·20	0·002	0·163	0·136	7·1
	24	¾	R	N E	36·39	0·15	0·0005	0·242	0·242	8 62
	29	¼	R	S W	11·12	0·10	0·001	0·588	0·294	4·97
November	7	1/10	R	N	13·7	0·25	0·003	0·436	0·326	5·68
	8	½	R	N W	20·6	0·30	0·002	0·242	0 097	7·1
	14	1/6	S	N W	30·1	0·30	0·008	0·68	0·388	14·20
	22	1/10	R	N	20·6	0·30	0·002	0·163	0·194	8·62
	23	2/5	R	E and N	11·12	0·05	0·001	0·34	0·34	7·1
December	13	1	S	W	27·0	0·25	0·009	0·136	0·114	7·1
	26	¼	R	N E	20·0	0·20	0·208	0·194	0·114	3·55
	25	3	S	N	8·5	0·20	0 003	0·388	0·294	14·20
January..	1	2	S	W	8·58	0·15	0·004	0·388	0·294	2·84
	4	⅕	R, S	N E	10·3	0·15	0·006	0·776	0·34	5·68
	12	4	S	N	11·67	0·50	0·003	0·436	0·194	7·1
	21	4	S	N	22·3	0·20	0·0005	0·097	0·057	7·1
	27	2	S	N E	17·5	0·35	0·002	0·388	0·057	7·10
February.	4	2	S	N E	13·0	0·10	0·001	0·163	0·163	4·62
	20	1/10	R, S	N	24·3	0·10	0·002	—	—	12·78
March ..	7	1/10	R	W	20 6	0·10	0·015	—	—	18 62
	10	¼	R	N E	14·2	0·30	0·024	0·872	0·68	2·84
	13	2	R	N W	29·14	0·30	0·003	0·388	0·163	7·1
	16	1	R	N W	12·06	0·15	0·004	0·136	0·194	9 94
April . ..	4	1/5	R	S	13·7	0·10	0·003	0·194	0·097	10·65
	7	4	S	N E	30·5	0·40	0·006	0·163	0·097	17·15
	16	3/10	R	—	22·3	0·15	0.002	0·776	0·294	7·1
	19	½	R	—	18·8	0·20	0·0015	0·242	0·114	2·84
	20	0·04	R	S	18·2	0·15	0·003	—	—	7·1
	20	0·03	R	S	11·8	0·10	0·001	—	—	5·68
	25	0·06	R	S	9·6	0·20	0·003	0·242	0·114	7·1
	29	¾	R	S E	13·4	0·30	0·008	0·242	0·163	7·1
	30	5/16	R	S E	17·5	0·15	0·004	0·163	0·136	7·1
May.. ..	4	½	R	S	6·8	0·20	0·002	0·436	0·294	12·78
	9	¼	R	N	4·3	0·10	0·001	0·163	0·136	7·1
	21	1/5	R	N E	14·2	0·30	0·003	0·114	0·097	5·68
	28	2	R	S E	7·6	0·20	0·004	0·294	0·194	8·62
	30	¾	R	S	11·12	0·10	0·002	0·163	0·163	7·1
	31	⅕	R	N W	13·0	0·10	0·001	0·114	0·097	7·1
June . ..	2	1⅔	R	S E	14·2	0·10	0·0005	0·242	0·163	5·68
	4	¾	R	E	20·0	0·10	0·0005	0·163	0·163	7·1
	5	⅔	R	S	8·6	0·10	0·001	0·114	0·097	7·1
	8	0·06	R	E	9·6	0·20	0·001	—	—	7·1

TABLE II.—*Pounds per Acre.*

tober..	20	½	R	W	0·15020	0·02268	0·00023	0·01849	0·01542	0·80540
	24	¾	R	N E	0·61420	0·02520	0·00008	0·04117	0·03226	1·46683
	29	¼	R	S W	0·06307	0·005671	0·00005	0·03335	0·01668	0·28639
November	7	1/10	R	N	0·03118	0·00567	0·00006	0·00999	0 00739	0·12886
	8	½	R	N W	0·28868	c·03361	0·00023	0·02745	0·01100	0·80540
	14	1/6	S	N W	0·11362	0·01120	0·00030	0·02574	0 01670	0·53693
	22	1/10	R	N	0·05773	0·00672	0·00004	0·00369	0·00430	0·19557
	23	2/5	R	E and N	0·10091	0·00045	0 00006	0·03089	0·03089	0·64432
ecember	13	1	S	W	0 61256	0·05671	0·00020	0·03085	0·02586	1·61081
	26	¼	R	N E	0·11344	0·00113	0·01180	0·01075	0·00646	0·20135
	25	3	S	N	0·04821	0·01514	0·00017	0·02151	0·01668	0·85540

TABLE II.—*Pounds per Acre* (continued).

Date.		Amount (inches).	Rain or snow.	Direction	Sulphate.	Nitrate.	Nitrite.	Nitrogen in free NH_3.	Nitrogen in alb. NH_3.	Chlorine.
January..	1	2	S	W	0·03244	0·00560	0·00015	0·01470	0·01112	1·28885
	4	½	R, S	N E	0·02946	0·00480	0·00018	0·02206	0·00966	0·16108
	12	4	S	N	0·08825	0·03560	0·00024	0·03330	0·01434	0·53693
	21	4	S	N	0·16864	0·01512	0·00003	0·00733	0·00431	0·53693
	27	2	S	N E	0·66172	0·01472	0·00008	0·01470	0·00431	0·26843
February.	4	2	S	N E	0·04915	0·00756	0·00004	0·00616	0·00616	0·17636
	20	1/10	R, S	N	0·05523	0·00226	0·00004	—	—	0·28994
March ..	7	1/10	R	W	0·05773	0·00226	0·00033	—	—	0·19557
	10	¼	R	N E	0·08079	0·01680	0·00136	0·09991	0·07724	0·16111
	13	2	R	N W	1·32224	0·13444	0·00136	0·17645	0·07396	3·22162
	16	1	R	N W	0·27361	0·03361	0·00091	0·03085	0·04302	2·25523
April . ..	4	1/5	R	S	0·62163	0·00453	0·00013	0·00860	0·00440	0·52325
	7	4	S	N E	0·23065	0·03025	0·00044	0·01028	0·00733	0·53693
	16	3/10	R	—	0·15177	0·01008	0·00135	0·02666	0·02001	0·48324
	19	½	R	—	0·21326	0·03361	0·00017	0·02745	0·00647	0·32221
	20	0·04	R	S	0·01652	0·00134	0·00002	—	—	0·06443
	20	0·03	R	S	0·01103	0·00068	0·00001	—	—	0·03865
	25	0·06	R	S	0·01306	0·00272	0·00004	0·00329	0·00155	0·09664
	29	¾	R	S E	0·22808	0·05041	0·00137	0·04367	0·02776	1·20811
	30	5/16	R	S E	0·01240	0·01050	0·00028	0·01280	0·01030	0·50338
May . ..	4	⅓	R	S	0·07713	0·02268	0·00023	0·04996	0·03336	1·44973
	9	¼	R	N	0·02414	0·00567	0·00006	0·00924	0·00771	0·40270
	21	1/5	R	N E	0·06463	0·01344	0·00012	0·00517	0·00440	0·25773
	28	2	R	S E	0·34485	0·09075	0·00183	0·13342	0·08604	3·91154
	30	¾	R	S	0·18921	0·01680	0·00030	0·02772	0·02772	1·20811
	31	½	R	N W	0·03686	0·00283	0·00003	0·00162	0·00275	0·20135
June . ..	2	1⅔	R	S E	0·70526	0·03780	0·00016	0·09150	0·06468	2·11407
	4	¾	R	E	0·33942	0·01680	0·00006	0·02772	0·02772	1·20811
	5	⅔	R	S	0·13163	0·01701	0·00013	0·00862	0·01433	1·07387
	8	0·06	R	E	0·01306	0·00272	0·00001	—	—	0·09664
					8·43565	0·89761	0·02466	1·14706	0·77429	32·33000

15·86 inches rain. 22 inches snow. Total = 17·69 inches rain.

A CONTRIBUTION TO THE THEORY OF SOLUTION.*

By E. J. HARTUNG, B.Sc.

(Continued from p. 276).

Theoretical Considerations.

IN attempting to establish a theoretical basis on which to consider experimental results one is met at the outset with the difficulty of expressing suitably the concentrations of the various substances present in the chosen mixtures. The molar fraction method recommends itself as being perhaps less open to objection than either the mass or the volume method of calculating concentration; in any case, it is the method which lends itself most simply to mathematical treatment from the mass action standpoint. However, one must remember that the molar fraction method is quite useless in the case of liquids in which the state of molecular aggregation in the liquid state is unknown. This will considerably limit in practice the application of a theory founded on it. In the following discussion the molar fraction method has been adopted.

Let us suppose we are dealing with two simple unassociated liquids A and B, the mixing of which results in the partial formation of a solvate $A_\alpha B_\beta$. Denison (*loc. cit.*) has shown, in the special case of a solvate AB_β, that the concentration of the solvate is a maximum when the liquid mixture has the synthetic composition denoted by the formula of the solvate. The proof can be extended to any solvate $A_\alpha B_\beta$. Thus we have—

$$\alpha A + \beta B \rightleftharpoons A_\alpha B_\beta.$$

Let N molecules of A be mixed with 1 − N molecules of B with the formation of x molecules of the solvate $A_\alpha B_\beta$. The total number of molecules present is—

$$1-(\alpha+\beta-1)x.$$

Applying mass action considerations, the equilibrium conditions require that—

$$(N-\alpha x)^\alpha(1-N-\beta x)^\beta = Kx[1-x(\alpha+\beta-1)]^{\alpha+\beta-1}$$

Differentiating this, we obtain—

$$\frac{dx}{dN} = \frac{(N-\alpha x)^{\alpha-1}(1-N-\beta x)^{\beta-1}[\alpha(1-N)-\beta N]}{K[1-(\alpha+\beta-1)x]^{\alpha+\beta-2}[1-(\alpha+\beta)(\alpha+\beta-1)x]+(N-\alpha x)^{\alpha-1}(1-N-\beta x)^{\beta-1}[\alpha^2(1-N-\beta x)+\beta^2(N-\alpha x)]}.$$

Hence—

$$\frac{dx}{dN} = 0 \text{ when } \frac{N}{1-N} = \frac{\alpha}{\beta}.$$

This means that, if we plot the number of molecules of solvate formed per one total synthetic molecule of the mixture against the number of molecules of A present per one total synthetic molecule, we obtain a curve which reaches a maximum at the concentration corresponding to the composition of the solvate.

Further, at one end of the curve (the pure B end) where N = 0 and $x = 0$—

$$\frac{dx}{dN} = \frac{1}{K+1} \text{ if } \alpha = 1;$$

$$\text{for any other value of } \alpha, \ \frac{dx}{dN} = 0.$$

At the other end of the curve (the pure A end), N = 1 and $x = 0$; therefore—

$$-\frac{dx}{dN} = \frac{1}{K+1} \text{ if } \beta = 1;$$

$$\text{for any other value of } \beta, -\frac{dx}{dN} = 0.$$

---

* A Paper read before the Faraday Society.

In words, if the formula of the solvate is the simplest possible, *i.e.*, if α and β each equal 1, the gradient of the solvate-concentration curve at the pure A end must be equal, but of opposite sign, to the gradient at the pure B end. If α has a value greater than 1, then the gradient at the pure B end is 0; similarly for β at the pure A end. If α and β are each greater than 1, then the gradients at both ends of the curve equal 0.

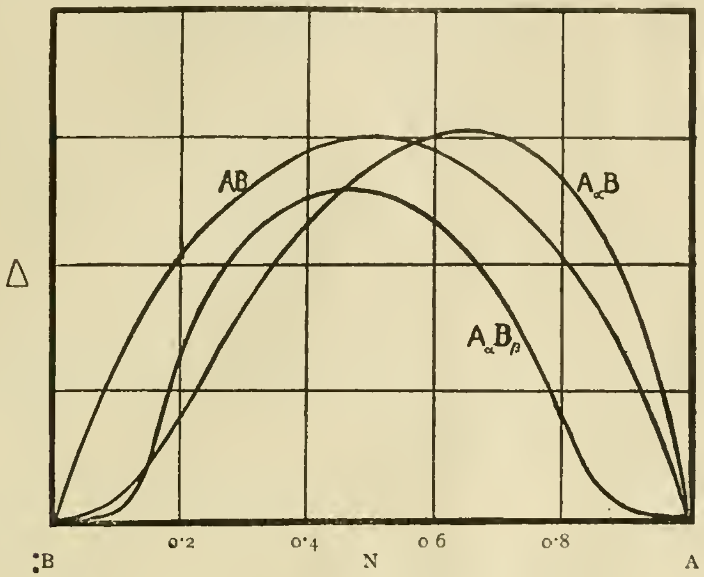

FIG. 3.

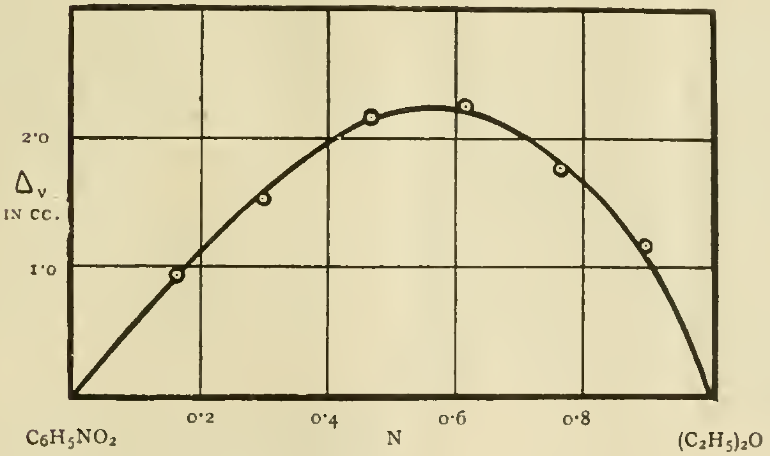

FIG. 4.

Now, it is easily shown that the extent of any deviation is directly proportional to the number of solvate molecules formed, or—

$$\Delta = kx,$$

where k is a constant depending on the molecular values for the particular property of A, B, and $A_\alpha B_\beta$ Hence the deviation curve also attains its maximum (or minimum in the case of negative deviations) point when—

$$\frac{N}{1-N} = \frac{\alpha}{\beta}, \text{ and again } \frac{d\Delta}{dN} = 0,$$

at both ends for any values of α and β respectively greate than 1; but—

$$\frac{d\Delta}{dN} = \frac{k}{K+1}$$

at the pure B end if $\alpha = 1$, and it equals $-\frac{k}{K+1}$ at the pure A end if $\beta = 1$.

Thus we have three types of curves (Fig. 3), representing the formation of solvates of the composition AB, $A_\alpha B$, and $A_\alpha B_\beta$ respectively. Obviously also the deviation curves for all properties of mixtures of a particular pair of liquids must, in general, be similar to each other.

For the simple case where $\alpha = \beta = 1$, the equilibrium equation simplifies to—

$$(N-x)(1-N-x) = Kx(1-x)$$

or—

$$x(1-x) = \frac{1}{K+1} . N(1-N).$$

Since $\Delta = kx$, it follows that—

$$k = \frac{\Delta}{1 - \frac{k}{K+1} \cdot \frac{N(1-N)}{\Delta}}$$

From this equation we can calculate k, the property constant, and K, the equilibrium constant, since values of N and Δ may be read from the curve, while $\frac{k}{K+1}$ is the gradient at each end of the curve and can be measured. Or, in order to avoid the inaccuracy of measuring tangents to the curve, we may solve the equation by treating k and $\frac{k}{K+1}$ as two unknown constants and choosing two values of N on the same property curve. Thus we can evaluate k and K, and, knowing k, we can calculate x values from those of Δ for any mixture and thus plot the true x curve. Further, we can treat different property curves of the same liquid-pair in this way and evaluate the k value for each, and they all should give the same x curve.

It is very doubtful whether any actual cases agree with the simple AB theory, as above, although some may be found to approximate to it closely enough to afford a test. Dolezalek and Schulze (*loc. cit.*) claim that mixtures of ether and chloroform supply such a case, but plotting of their results shows a considerable deviation from perfect symmetry, although this is neglected by them. Notwithstanding Denison's argument to the contrary, it seems probable that, in most cases, two or more solvates are formed, and it becomes very difficult to apply a simple working theory quantitatively. The deviation curves for many pairs of unassociated liquids are quite different for different properties of the same pair, and this makes an explanation on a single solvate basis quite impossible. The assumption of the presence of two or more solvates in such cases gives a satisfactory qualitative explanation at least, for then the deviation curves would be compounded from two or more variables.

A quantitative explanation is not yet possible, because the equations obtained by applying mass action considerations contain several constants for which values cannot be calculated. However, by assigning arbitrary values to these constants it is possible to calculate deviation curves which approximate closely to those obtained by experiment. Further, it is improbable that only one solvate will be present in a given mixture, because the original solvate formed must have some tendency to combine with further molecules of one or both pure components, with the formation of new solvates. Repetitions of this process are possible, but the concentrations of these higher solvates will probably be so small as to be inappreciable.

Throughout the foregoing argument solvate formation alone has been considered, and no account has been taken of changes in the state of association of the component liquids on mixing. This limits the testing of the theory in practice to the examination of mixtures of known unassociated liquids, in which mixtures one may reasonably suppose solvate formation to be the predominating factor. In the case of associated liquids it is extremely difficult to develop a satisfactory quantitative theory, owing to the complexity of the phenomena. Dolezalek (*loc. cit.*) has made an attempt to do so in the case of very simple mixtures, but his method can have only a very limited application.

Discussion of the Results.

For various reasons the choice of suitable experimental liquids has been somewhat limited. A few words are necessary as to the suitability of the liquids actually chosen for the testing of the solvate theory. Ether is well known as a typical unassociated liquid.

Aniline and nitrobenzene are found by Dutoit and Mojoiu to be slightly associated (*Journ. Phys. Chim.*, 1909, vii., 169), while the Ramsay and Shields' method indicates that both liquids are normal or slightly dissociated (*Trans. Chem. Soc.*, 1893, lxiii., 1089). Also Beckmann finds that the molecular weight of aniline dissolved in ether is normal (*Zeit. Phys. Chem.*, 1889, iii., 603).

Methyl alcohol is well known to be strongly associated, the association factor by Ramsay and Shields' method being 3·43.

Carbon tetrachloride is found to be normal by Dutoit and Mojoiu (*loc. cit.*), and this is also indicated by the Ramsay and Shields method. Dolezalek (*Zeit. Phys. Chem.*, 1908, 64), on the other hand, calculates a value 1·15 at 50° for the association constant, which fits in with his theory of the conditions obtaining in mixtures of carbon tetrachloride and benzene.

The following symbols are used in the tables of results:—

M, the percentage by weight of the more volatile component in the mixture.
N, the number of molecules of this component per one total synthetic molecule of the mixture.
D, the density of the mixture at the temperature of experiment, referred to water at 4°.
V, the molecular volume of the mixture in cc.
S, the specific heat of the mixture.
C, the molecular heat of the mixture from a smooth curve).
E, the heat change on mixing per 100 grms. of the mixture, in calories.
Δ_v, the contraction in volume of the mixture on mixing per one total synthetic molecule, in cc.
Δ_c, the rise in molecular heat on mixing, in calories.
Δ_E, the heat change in calories on mixing per one total molecule of the mixture, positive or negative as indicated.

Nitrobenzene and Ether.

The experimental results for this liquid-pair are given in the following tables:—

TABLE I.—*Contractions at 20°.*

M	N.	D.	V.	Δ_v.
0	0	1·20369	102·23	0
10·35	0·1609	1·13401	101·55	0·93
20·21	0·2962	1·07293	101·17	1·54
34·34	0·4649	0·99462	100·83	2·17
48·85	0·6134	0·92116	100·98	2·26
65·87	0·7623	0·84297	101·69	1·78
84·21	0·8985	0·77099	102·52	1·18
100	1·0000	0·71322	103·87	0

TABLE II.—*Heat Capacity at 20°.*

M.		S.	C.	Δ
0	0	0·342	42·1	0
10·35	0·1609	0·362	41·7	0
20·21	0·2962	0·382	41·5	0
34·34	0·4649	0·408	40·9	−0·2
48·85	0·6134	0·443	41·2	+0·3
65·87	0·7623	0·473	40·5	+0·1
84·21	0·8985	0·512	40·5	−0·2
100	1·0000	0·540	40·0	0

The heat change on mixing was found to be very small, and no systematic series of measurements of this property was made.

The curve obtained by plotting Δ_v against N is shown in Fig. 4. It will be seen that, although the contraction on mixing is considerable, the heat capacity shows practically no deviation from the mixture law. Also, the heat change on mixing is very small. A simple inspection of the contraction curve makes it clear that more than one solvate must be formed in this case, since the curve is not symmetrical and does not reach a maximum at N = 0·5 (thus disposing of the simple A B supposition), and also since the gradients at both ends of the curve have definite values (thus disposing of the A_aB_b supposition). However, the experimental results are too meagre to permit further conclusions to be drawn.

(To be continued).

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

Part II.—Liquids.

By IRVING LANGMUIR

(Continued from p. 276).

Before beginning an experiment the air blast is started, impurities on the surface H are blown to the other side of B, and this surface of the water is cleaned by scraping with a strip of paper, C. All contaminating films are thus forced into the space L, from which they may be removed on to small pieces of paper dipped into the water. The air pressure or the balance is so adjusted that the centre of the edge of the strip B is directly below the point J, which is fastened to the end of the metre stick M.

A weight of 50 mgrms. is placed on the pan of the balance. This causes the rods R with the strip B to move (to the left in the diagram) until they strike a stop, which is not shown in the figure. The strip A is placed on the surface and is moved along until it is close to the strip B, to see if there is any residual contamination of the surface. Usually when A is brought within 5 to 10 mm. of B the latter is caused to move along with A because of residual contamination. When the edge of the strip is under the point J the force exerted by the oil film must be equal to the weight in the pan P, multiplied by the ratio of the lever arms of the balance (about 1 : 3). The distance between the strips A and B is then read off on the metre stick M, avoiding parallox by observing the reflection in the water surface. In this way the amount of residual contamination is determined. Owing to oil contained in dust in the air which settles on the surface, and to oil which adheres to the sides of the tray from previous experiments, it is difficult to entirely avoid this contamination. However, by scraping the surface a few times after each experiment the amount of this contamination can be reduced to less than 1 cm. with 50 mgrms. on the pan, or one or two mm. with 500 mgrms. This amount is practically negligible.

After thus making sure that the surfaces are clean one or two drops of the benzene solution are placed on the water between A and B and a 50 mgrm. weight is placed on the pan. Strip A is then moved along until the oil film produces sufficient pressure against B to bring it under the equilibrium point J. A reading on the metre stick is taken. Then another 50 mgrms. weight is applied and the strip A is again moved until equilibrium is reached. Weights of 50, 100, or 250 mgrms. are thus added successively until the oil film has been compressed into a space of a few millimetres.

As a result of these measurements the force acting on the strip A may be plotted as a function of the area included between the strips A and B. A typical curve is that shown in Fig. 7.

The weights applied to the pan are plotted as ordinates while the distances in cm. between A and B are plotted as abscissæ.

When the area is greater than a certain rather definite limit, Q, there is practically no force acting on the balance, but as the area is decreased the force rapidly increases until it reaches a limiting value at the point H.

Both solid and liquid films were studied. With such a substance as palmitic acid the surface of the water (as evidenced by dust particles) remains mobile only until the point S, Fig. 7, is reached. The whole surface then becomes rigid, that is, all dust particles on the surface become fixed in their relative positions. As the film is compressed beyond this point the whole surface moves as an elastic membrane. The film itself, however, remains entirely invisible until a point beyond H is reached, when the solid surface begins to crumple and a peculiar appearance (strain lines) is often observed on the surface.

On the other hand, liquid films, such as those produced by cetyl alcohol, or oleic acid, preserve their mobility even when compressed up to very small fractions of their original areas.

After a solid film has been crumpled up beyond the point H it will not expand again upon removing the pressure. The liquid films will spread out, but with marked hysteresis effects. To avoid these all the measurements were made in regular sequence increasing the weights by regular increments. However, the curves obtained by adding 50 mgrms. at a time were usually not materially different from those formed with 250 mgrm. increments.

Experimental Results on the Forces Required to Compress Surface Films.

A large number of fatty acids, alcohols, and esters have been studied by this method. Some of the results are given in Figs. 8 to 18. The curves are based on observations like those represented in Fig. 7, but the co-ordinates are expressed in different units. The areas of water covered by the films were divided by the number of molecules of oil added, and the areas per molecule in sq. cm.

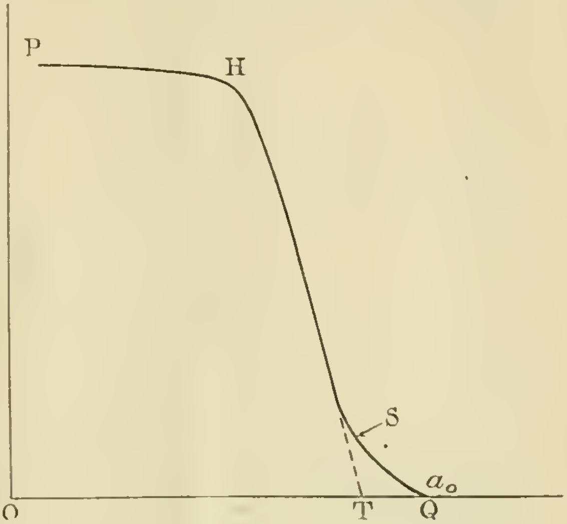

Fig. 7.

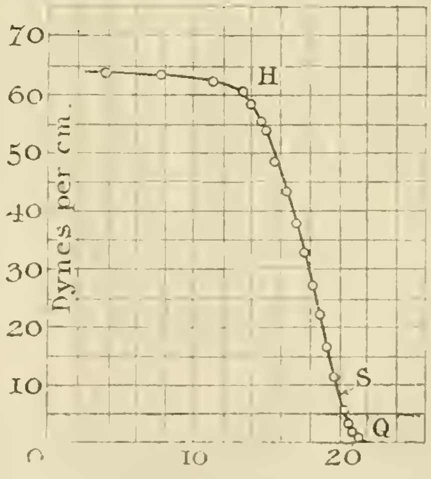

Fig. 8.—Palmitic Acid on Water at 16° C.

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* From the *Journal of the American Chemical Society* xxxix., No. 9.

were thus calculated. These are plotted as abscissæ, while the forces acting on the films are expressed in dynes per cm. and are plotted as ordinates. The unit used for the abscissæ of the curve is 10^{-16} sq. cm. per molecule.

In referring to these and similar curves in the following discussion we shall use a to denote areas per molecule and F to denote the force in dynes per cm. with which the film resists compression. The co ordinates of any particular point on the curve we shall indicate by subscripts, thus the co-ordinates of the point H in Fig. 7 are F_H and a_H. The letter H is is used to denote a kink in the curve at which the slope (as a decreases) becomes *horizontal* or nearly so. The letter V denotes a kink where the slope suddenly increases so that the curve tends to become *vertical* (for example in Fig. 11). The value of a corresponding to the point O will be usually denoted by a_0, since the ordinate of this point is $F = 0$.

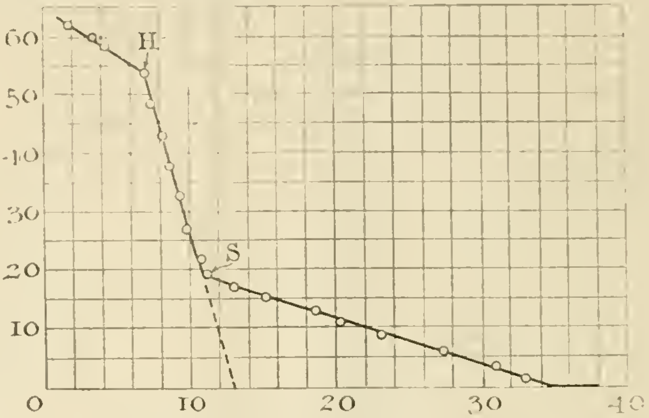

Fig. 9.—Palmitic Acid on Water at 45°.

The substances studied by this method included acids, alcohols, and esters of saturated and unsaturated aliphatic hydrocarbons.

The materials used differed very considerably in purity. The samples of lauric, palmitic, stearic, and oleic acids, and the ethyl palmitate were of high purity, and were kindly given by Prof. W. D. Harkins. Arachidic, myristic, cerotic and erucic acids, cetyl and ceryl alcohol, ethyl palmitate, amyl stearate, and cholesterol were furnished from the chemical museum of Columbia University through the kindness of Prof. J. L. R. Morgan. The amyl stearate, arachidic acid, and ethyl palmitate appeared to be of high purity, but the erucic and myristic acids and cholesterol were of doubtful purity. Samples of myricyl alcohol, cerotic acid, cetyl alcohol, and cetyl palmitate, and oleic acid, of a high degree of purity, were prepared in this laboratory by Mr. Harold Mottsmith. Samples of myricyl and cetyl alcohols, oleic, cerotic, myristic, arachidic, and linoleic acids were purified by fractional distillation in very high vacuum (pressure lower than 0·0001 mm. of mercury). Samples of linoleic and linolenic acids from a well-known manufacturer (in sealed tubes) were also available. The specimens of triolein, trielaidin, tristearin, and ricinoleic acid were prepared by Mr. Mottsmith without attempting to get very high purity. Samples of oil such as linseed, cotton-seed, soya bean, &c., purified by his special process were kindly furnished by Dr. Charles Baskerville.

Saturated Acids.—Lauric ($C_{11}H_{23}COOH$), myristic ($C_{13}H_{27}COOH$), palmitic ($C_{15}H_{31}COOH$), stearic ($C_{17}H_{35}COOH$), arachidic ($C_{19}H_{39}COOH$), and cerotic ($C_{25}H_{51}COOH$) acids were invesigated. Lauric acid proved too soluble in water for reliable measurements, the films contracting in area during the course of the measurements. Myristic acid showed some indications of solubility, but not enough to interfere seriously with measurements. The curve obtained with a film of pure palmitic acid on distilled water at 16° is given in Fig. 8. The point marked S is that at which the film became solid.

The value of a_0 is about $21{\cdot}8 \times 10^{-16}$.

The force necessary to compress the film to $a_H = 13 \times 10^{-16}$ sq. cm. is about $F_H = 63$ dynes per cm. This is nearly as great as the surface tension of pure water (73 dynes per cm.).

The curves obtained with stearic, arachidic, and cerotic acids on pure water at 16° were in all respects practically identical with those found for palmitic acid (Fig. 8).

Upon cooling the water to 4° the curves still remained unchanged. With the water at 45° the curve for palmitic acid (but not the higher fatter acids) changed to the form given in Fig. 9. Up to the point marked S the film remained liquid. Evidently then the melting point of the film is a function of the area available per molecule. At this higher temperature the value of a_0 for palmitic acid is very materially greater than at lower temperatures, namely, 34×10^{-16} instead of $21{\cdot}8 \times 10^{-16}$ sq. cm.

(To be continued).

COMMITTEE ON THE NEGLECT OF SCIENCE.

(Concluded from p. 279).

4. *Conference of Five Associations.*

In August, 1916, representatives of literary, historical, and geographical studies issued the following memorandum to the Press:—

The following resolutions, drawn up by a Conference, representative of the five associations concerned, have received the approval of the Councils of the Classical, English, Geographical, Historical, and Modern Language Associations. They are intended to form a basis for common action by the five associations as well as, it is hoped, for co-operation with representatives of the mathematical and natural sciences and of other elements in education. It must, therefore, be understood that they do not represent the full views of the associations concerned, but rather a common measure of their views, which they all accept as a basis. In the same way the propositions laid down do not profess to cover the whole field of education, but are limited to the spheres with which the five associations directly deal. Some apology, moreover, seems needed for the use of such contrasted terms as "humanistic" and "scientific." They are simply employed for the sake of brevity, for all would agree that "humanistic" studies should be scientific, and "scientific" studies humane.

The resolutions are now published in the hope that in any coming reconstruction of our educational system this attempt to restate the "humanistic" position will mitigate the dangers incident to a violent breach of tradition and an excessive reaction against the past predominance of certain types of study.

It will be obvious that they are drawn up in no spirit of hostility or indifference to either scientific or technical studies. Their framers are anxious to co-operate in securing for these, as well as for the studies in which they are themselves more particularly interested, their due place in a national system of education.

Pending the formation of some central council, which could assume a larger responsibility and speak with a wider representative authority, they would welcome offers of co-operation or suggestions for the further practical development of the position taken in these resolutions.

Any communication may be addressed to the Chairman of the Conference of the Five Associations, Prof. Tout, 1, Oak Drive, Fallowfield, Manchester.

The resolutions are as follows:—That in the opinion of the conference—

(i.) It is essential that any reorganisation of our educational system should make adequate provision for both humanistic and scientific studies.

(ii.) Premature specialisation on any one particular group of studies, whether humanistic or scientific, to the exclusion of all others is a serious danger, not only to education generally, but to the studies concerned.

(iii.) Humanistic education implies the adequate study of language and literature, geography, and history, which in each case should, at the appropriate stage of education, go beyond the pupil's own language and country.

(iv.) The representatives of humanistic studies would welcome from the representatives of the mathematical and natural sciences, a statement with regard to those studies similar to that contained in (iii.).

(v.) In all reform of education it must never be forgotten that the first object is the training of human beings in mind and character, as citizens of a free country, and that any technical preparation of boys and girls for a particular profession, occupation, or work must be consistent with this principle.

(vi.) Subject to the above principles the associations concerned would welcome a comprehensive revision of national education from the point of view of present needs.

BRYCE. FREDERIC G. KENYON.	On behalf of the Classical Association.
CROMER. JOHN BUCHAN.	On behalf of the English Association.
DOUGLAS W. FRESHFIELD. H. J. MACKINDER.	On behalf of the Geographical Association.
C. H. FIRTH. T. F. TOUT.	On behalf of the Historical Association.
EDMUND GOSSE. HERBERT WARREN	On behalf of the Modern Language Association.

Representatives of the five associations referred to above afterwards combined with a committee of the British Academy to form an organisation called the Council of Humanistic Studies, with Lord Bryce as President and Sir Frederic Kenyon as Secretary. In a letter to the Secretary of the Committee on the Neglect of Science, Sir Frederic Kenyon said:—"Our object is practically identical with yours. I believe (and these are the views we have adopted) not only that there is room for an increase in the time and attention given to natural science, but that such an increase is eminently desirable; that a sound elementary education ought to include *for all* a good grounding in languages and literature (ancient and modern), history, mathematics, and natural science; that early specialisation should be discouraged, but that boys should do progressively more of the subject for which they have most aptitude, without wholly dropping the others, at any rate until quite near the end of their school course."

5. *Joint Conference.*

A joint meeting of representatives of Lord Bryce's Council and the Committee on the Neglect of Science was held on December 8, 1916. Sir Ray Lankester read the resolutions passed by the meeting held on May 3, 1916, and also the following resolutions in extension of them, adopted by the Committee:—

This Committee, in accordance with the resolutions passed at the meeting on the Neglect of Science, held on May 3, 1916, desire to make clear the following points:—

1. That their essential object is to secure for the teaching of natural science a position of no less importance, as an essential component of a liberal education, than that which is now held by the teaching of languages and history.
2. That, although they make no proposal to displace these subjects from the curriculum of public schools (*i.e.*, the schools represented at the Headmasters' Conference) they recognise that for the attainment of their object it is necessary that time now spent on the study of Latin and Greek grammar and composition and of Roman and Greek history must be greatly diminished.
3. That it is necessary that the position of a boy on entering the school, and in later years, should no longer be determined mainly, as it is now in many schools, by his proficiency in "Classics."
4. That the classical teachers should not be more numerous nor more highly remunerated than those engaged in teaching the natural sciences; in fact, a good form-master should be able to teach boys both natural sciences and literary subjects.

Sir Ray Lankester referred particularly to the need not merely for "some" science in the curriculum but to secure for the natural sciences an integral place of capital importance—that is, equal to that of any other group of studies. With this end in view, the following general division of a school week of thirty-six periods was suggested:—

English, including history..	9
Languages other than English	9
Natural Sciences, including geography..	9
Mathematics, including mensuration ..	6
Drawing, manual work, &c.	3

The Conference finally adopted the following resolutions:—

1. That in all schools in which education is normally continued up to or beyond the age of sixteen, and in other schools so far as circumstances permit, the curriculum up to about the age of sixteen should be general and not specialised, and that in this curriculum these five groups of subjects should be integrally represented:—

(i.) Languages other than English.
(ii.) English and history.
(iii.) Mathematics.
(iv.) Natural sciences, including geography. (It is understood that geography would also be taught in connection with history).
(v.) Artistic and manual training.

2. That the representatives of the "Council for Humanistic Studies" be asked to collect the opinions of their constituent associations as to the proposal of the "Neglect of Science Committee," that the ratio of the five elements of a general education up to the age of sixteen, expressed in school periods devoted to them be—Languages, 3; English and history, 3; mathematics, 2;

natural sciences and geography, 3; artistic and manual training, 1. It is understood that the ratio extends over the whole curriculum, and is not necessarily that of a single term or school year, and is subject to the proviso expressed in the footnote to Resolution (1).

3. That the Committee on the Neglect of Science be asked to prepare a statement as to the aim of the teaching of natural science in secondary education and as to the specific subjects (if any) which should be comprised in the curriculum, having regard to the distinction between "equipment" subjects and those of a more generally educational character.

The opinions of the five associations represented at the Conference, upon the suggestions contained in Resolution (2) above, were communicated by Sir Frederic Kenyon to the Secretary of the Committee on May 6, 1917, and are as follows:—

Classical Association.

The Council of the Classical Association, while agreeing that more time should be devoted to natural science in many schools of the older type, are not prepared to accept the time-table put forward by the "Neglect of Science" Committee. They consider it a grave mistake to attempt to bind educational authorities to a fixed allotment of school hours. They consider, further, the suggested grouping of subjects to be unscientific; and while the time allotted to classics (which appear only as part of a group including modern languages) is manifestly too little, in view of their difficulty, the time allotted to natural science is largely in excess of that contemplated in the specimen curriculum put forward by the Association of Public School Science Masters.

The Council are of opinion that real assistance can be given to schoolmasters by the associations representing various branches of knowledge, by indicating the spirit in which their several subjects should be studied, and what particular portions of them should be included in the curricula of secondary schools, whether in their general or their more specialised stage; but they think it is not within their legitimate sphere of action to prepare time-tables or to prescribe allowances of hours, especially with regard to subjects other than their own.

English Association.

The Executive Committee at their last meeting had under consideration your request that they should express their opinion on the question of the distribution of a thirty-six hours time-table into nine hours for science, nine for English, nine for other languages, six for mathematics, and three for manual training. The Committee came to the conclusion that it did not come within their province to lay down any definite allocation of time for the various subjects, and that this must be left to the discretion of the headmasters and headmistresses of the schools.

Geographical Association.

The Council of the Geographical Association have had before them the minutes of a joint conference, held at the Royal Society on December 8, between representatives of the Council of Humanistic Studies and of the Neglect of Science Committee.

The Council of the Geographical Association are agreed that natural science should have an integral place more important than hitherto in the time-tables of the schools, but they are opposed to laying down any definite apportionment of hours to subjects. They would prefer a statement of what should be expected of the average boy or girl at the age of sixteen.

In regard to the note which has been added to the first and second resolutions passed by the joint conference, to the effect that geography would also be taught in connection with history, they would direct attention to the statement sent herewith, which they have unanimously adopted, putting forward the aims which teachers of geography have in view. They feel that it is essential that geography should be taught as a single subject, and should not be divided between the teachers of natural science and history.

Historical Association.

1. The Historical Association cannot accept as a basis of agreement that five-twelfths of the school time for boys and girls up to the age of sixteen should be devoted to natural science and mathematics.

2. In the opinion of the Council of the Historical Association out of the periods assigned to English not less than three should be given to history alone.

Modern Language Association.

A modern language requires a daily period—*i.e.*, not less than five periods a week—during the first two years; after that four periods are sufficient.

. A second language should not be begun until two years after the first is begun.

In justification of the suggested general allocation of school periods for groups of subjects put before the Joint Conference on behalf of the Committee, it should be said that the relative fractions were arrived at after careful consideration of time-tables and modern needs. As to the grouping, it may here be mentioned appropriately that the Board of Education's scheme for Secondary Schools Examinations adopts the following division of subjects:— For the Junior Examination (ages 16+) (1) English subjects, (2) Foreign Languages, (3) Science and Mathematics; for the Senior Examination (ages 18+) (1) Classics and Ancient History, (2) Modern "humanistic" studies, (3) Science and Mathematics.

In response to the request contained in Resolution 3 of the Joint Conference, a Memorandum on the aims of the teaching of natural science was drawn up, and after approval by the Committee was sent to Sir Frederic Kenyon for distribution to the representatives of his Council present at the Conference, together with copies of a scheme of work in "Science for All," issued by the Association of Public School Science Masters. The Memorandum was as follows:—

Aims of the Teaching of Natural Science in Secondary Schools.

As misconception still exists as to what subjects are included in the term "Natural Sciences," it may be well to state that here the term signifies all departments of natural knowledge which depend for their development upon observation and experiment. It comprises therefore both the physical and the biological sciences of any branch of them.

Among the aims of the teaching of science as thus defined are: (1) To train the powers of accurate observation of natural facts and phenomena and of clear description of what is observed. (2) To impart a knowledge of the method of experimental inquiry which distinguishes modern science from the philosophy of earlier times, and by which advance is secured. (3) To provide a broad basis of fact as to man's environment and his relation to it. (4) To give an acquaintance with scientific words and ideas now common in progressive life and thought.

Experience shows that when scientific knowledge has been secured by practical work it becomes part of the permanent mental equipment of the pupil. Scientific method can be used in the study of literary, historical, and other subjects; but applied in this way it can never be accepted as providing the same means of training as direct observation and experimental work. The laboratory is the place where the pupil learns to acquire first-hand evidence and to distinguish between it and information obtained verbally or by reading; for this reason it alone fulfils an essential function in education. But while prime importance must be attached to training in personal observation and experiment, it is essential that there should also be instruction in the broad principles and results of investigation, in order to produce appreciation of the human aspects of scientific discovery. Modern scientific progress is just as much an achievement of thought as any other movement, and no science course is complete which does not present it as a humanistic study in the fullest sense.

It would be most undesirable to specify the subjects which should be studied in a course of instruction in natural science in schools as a part of general education. (The objection is to the laying down of a detailed syllabus of work to be done in all Secondary Schools, rather than than to the broad statement of subjects which should be included in the curriculum. A prescribed syllabus which limits the freedom of the teacher and stereotypes the work of schools should be avoided). It should be sufficient to say that, before systematic work is commenced in the laboratory, there should usually be a course of observational study intended to direct attention to common facts of earth and sky, animal and plant life, and natural phenomena generally. In addition, a course of practical measurements illustrating the teaching of arithmetic may be best undertaken at this stage. Laboratory work should be commenced after the observational course, and at all stages there should be descriptive lessons or reading covering a much wider field of human scientific activity than can be surveyed from the laboratory bench. A scheme of work which takes account of these broad ideas has been drawn up by members of the Association of Public School Science Masters on the basis of what is actually done in one of the great public schools. This syllabus is submitted as suggesting suitable subjects for general courses of scientific study, but it should be regarded as an example rather than a prescription to be used by all schools.

No formal communication has been received from the five associations with reference to this Memorandum, but Sir Frederic Kenyon has suggested that an agreement might be arrived at as to what should constitute a course of school science by adopting the general lines of the syllabus of the Association of Public School Science Masters. As, however, it is understood that a Committee of the British Association will include several schemes of work of a similar kind in a Report on Science Teaching shortly to be issued, and suggestions as to suitable work will also probably be made by the Government Committee on Science, it seemed best to defer further discussion of the subject at another joint conference until these Reports are available.

It will be observed that the Committees of the several associations represented by Lord Bryce's Council are very far from agreement with the Committee on the Neglect of Science. They do not even accept the resolutions agreed upon by the Conference of Lord Bryce's Council with the Committee on the Neglect of Science

At the request of Mr. W. A. Bulkeley-Evans, Secretary of the Headmasters' Conference, a copy of the Memorandum upon the aims of the teaching of natural science was sent to each of the 120 members of the Conference.

6. *Publications.*

Early in the present year Sir Ray Lankester, acting on behalf of the Committee, arranged with Mr. W. Heinemann for the publication of a reprint of lectures on "Science and Education," delivered at the Royal Institution in 1854, with an introduction and notes by him. The Committee considered that a useful purpose would be served by bringing this volume before the notice of its subscribers, as the lectures dealt from various points of view with the advantages to be derived from attention to the natural science in education. A copy of the book was sent, therefore, to each subscriber to the funds of the Committee, together with six copies of the Report of the Proceedings of the meeting held on May 3, 1916.

The Committee has arranged for the publication by Messrs. Longmans, Green, and Co. of a volume entitled "The Public School System in Relation to the Coming Conflict for National Supremacy," by Mr. V. Seymour Bryant, Assistant Master at Wellington College. The volume contains an excellent statement of the positions of subjects taught in preparatory and public schools, with particular regard to the prominence given to Greek and Latin studies, and the unsatisfactory position occupied by natural sciences. When the book is published a copy will be sent to each subscriber to the funds of the Committee.

7. *Essential Objects of the Committee.*

Several communications have been received from organisations concerned with professional aspects of education, and the Committee has been able to afford assistance to such bodies in the way of providing information. The Committee is of the opinion, however, that its activities are best limited to the advocacy of adequate attention to the natural sciences in the public schools and at Oxford and Cambridge, and to securing for them a prominent place in the examinations for the public services. These matters define clearly the work of the Committee, and are not the objects of any other organisation. While, therefore, the Committee is aware of desirable changes in the position of science in schools of all grades and in national affairs generally, it believes that the best means of effecting reforms in all directions will be the securing of adequate attention to science in the education of students at the public schools and Universities, where a large number of the most influential members of the community receive their early training. Its activities will be continued until these ends have been attained.

Signed on behalf of the Committeee on
the Neglect of Science,
E. Ray Lankester.
A. S. E. Ackermann.
R. A. Gregory.

THE TUNGSTEN DEPOSITS OF ESSEXVALE, SOUTHERN RHODESIA.

There seems to be a general opinion that the tungsten deposits of Essexvale consist only of so-called alluvial or rubble, wolframite, and that reefs have not been found. This is not true. Some reefs have long been known, and the excavation of the rubble has led to the uncovering of others, which, so far as can be judged without actual sampling and development, offer good prospects for mining. But hitherto there has been a strange reluctance to undertake mining operations on the reefs, whilst the work on the rubble has been largely desultory.

Position.

The known tungsten reefs lie within an east and west rectangular block of country of about nine and a half square miles area, immediately to the north of Essexvale Siding and mainly west of the railway. The reefs extend from the neighbourhood of "The Ranche" (2¾ miles north-west of the siding) to the native church (1½ miles north-east of the siding). Sixteen distinct reefs are known, eleven of which have had a little work done on them from time to time.

History.

The deposits were first prospected in 1906. In the ensuing two years a fair amount of ore was produced, but in 1909 the production ceased. A little interest was again taken in the deposits in 1912-13, but there was no production in 1914-15. At the end of that period a local syndicate extensively sampled some thousands of tons of rubble and made trial crushings. The grade was found to be just too low for profitable working by the methods then employed. During 1916, however, determined efforts have been made by other workers to test the rubble of two restricted areas.

Altogether about 85 tons of concentrate, valued at £7165, has been marketed. The returns for 1916 are 2½ tons, valued at £467. This was produced by one worker with a few natives in a 5-ft. rotary diamond washer, and by one man on another claim, who hand picked rubble and recovered 1600 lbs. of wolframite.

The prospecting done on a few reefs that have been opened has nowhere been for more than a few feet below the surface. This may be due chiefly to the fact that the deposit upon which serious prospecting work has been undertaken is from its nature the least likely to prove profitable.

Geology.

The known tungsten-bearing tract of country occupies the central portion of an irregularly oval mass of granite about 8 miles long and 5 miles across at the widest part. The long axis of the mass trends north-west to south-east. This granite body forms the floor of a wide depression which is traversed by two permanently flowing streams, one of which is known as Fern Spruit. The granite appears to pass beneath the surrounding rim of epidiorite and felsite hills. The soil is a pale red sandy loam. There are very few exposures excepting in the streams and an occasional small but bold granite kopje. The granite almost wherever seen is coarse-textured and massive—that is, not schistose. It is a hornblende granite, and is thus different from the large granite masses of Rhodesia. Patches of epidiorite, probably inclusions of country rock, and dykes, and other bodies of felsite, are occasionally encoontered, particularly near the eastern edge.

The Reefs.

The tungsten reefs consist of greisen composed chiefly of a soft greenish yellow mica, or of mica, fluorspar, topaz, and secondary felspar. This rock weathers soft and rusty brown. The greisen has arisen by the action of vapours on a porphyry or aplite (fine-textured white granite free from hornblende and mica). With the greisen of each reef is a variable amount of rather white glassy quartz forming strings or large lenses in the greisen, and evidently connected with the greisenisation—that is, deposited at the same time and by the same agency as the mica, fluorspar, topaz, tourmaline, chlorite, wolframite, and scheelite of the greisen.

The constant presence of the quartz lenses as part of the greisen bodies is a great help in recognising the presence of the greisen. Those parts of the greisen which contain little or no quartz very rarely crop out, and thus may easily escape discovery. No tungsten reefs have been found without the quartz, although it is quite conceivable that such exist.

The quartz strings expand into lenses exceeding 20 ft. in width, and thus make low hillocks such as those at "The Ranche" homestead; again, two-thirds of a mile to the south-east of this, and at the native church a mile and a half north-east of Essexvale Siding.

The reefs vary from 200 yards to about a mile long. The two most promising reefs exposed are respectively about a mile long and half a mile long so far as proved. These are the Rhoda reef in the north-eastern portion of Plot 27, and the reef running through the Lunar and Moon blocks near the common boundary of Plots 37 and 38.

With one exception the reefs examined strike east to west, and dip north at angles varying between 30° and 55°. The reef on Plot 4 strikes north-west to south-east and dips north-east at 53°.

The width of the reefs is, of course, variable owing to the lenses of quartz. Apart from the quartz lenses, the width averages 3 feet, and is surprisingly constant.

In each instance the country is coarse massive hornblende granite without signs of shearing or faulting between the reef and the country. It appears therefore that the aplite was injected along master joint planes caused by the contraction of the granite on consolidating, and not in fissures caused by faulting. This may have an important bearing on the persistence of the greisen bodies below the surface. In a few instancss the mica greisen has a slightly schistose appearance. In a few places greisenisation of the country is suspected, but this is on a small scale only, and no tungsten ore has been discovered in it.

With the exception of the Union Jack reef in the north-west corner of Essexvale Reserve, the aplite has been completely greisenised so far as can be judged by the small amount of reef exposed. At the Union Jack the intrusion exceeds 6 ft. in width, but about a third of it consists of white aplite apparently ungreisenised.

Stockwork Deposit.

The block upon which most work has been done differs from the above blocks, which may be taken to be normal. The occurrence in question is situated on Tungsten Kopje, a prominent hill of massive hornblende granite with a low ridge extending about 300 yards to the east and a longer one to the west.

The fact that a large amount of float wolframite occurred immediately around the hill led to prospecting on the hill, with the result that a stockwork deposit was discovered extending along the eastern and western ridges, and on the north flank of the hill.

Throughout the massive hornblende granite of this zone streaks and seams of aplite containing gashes of quartz are scattered rather sparsely and quite indiscriminately. These seams run in all directions and at all angles; many are nearly flat, but some are vertical; they make small saddles in several places, but pursue irregular courses, and expand and die out quite irregularly. They average a few inches wide, and in no instance exceed a foot. None are traceable for more than a few yards. The greisen always carries streaks of quartz, and occurs on one or both sides of the latter. The aplite varies in degree of greisenisation. In some parts the greisen consists of sugary quartz and pyrite with very fine wolframite scattered through it but invisible to the naked eye. Such a rock weathers brown, and strongly resembles sandstone. It is always present in the rotary concentrate. In other parts the greisen consists chiefly of a soft yellow mica.

At the south-west end of this deposit a body of greisen about 6 ft. wide, striking north to south, and dipping about 40° E., has been opened, and afforded rich patches of wolframite.

Minerals of the Greisens.

The minerals detected in the greisens comprise quartz, soft yellow mica, felspar, dark green chlorite in rosettes, black tourmaline, pyrite (altered to cubes of limonite at the surface), fluorspar (blue, mauve, green, white, and colourless), topaz (pale brown and colourless), galena (rather rarely), pyrrhotite, wolframite, and scheelite.

Small quantities of each of these occur in the quartz. Here and there a bunch or streak of any one of them, including the tungsten minerals, lies in the quartz. The distribution of the minerals in the quartz or in the altered aplite is, in fact, generally patchy, as is always the case in greisens. Coarse aggregates of any one mineral are occasionally noted—for example, single aggregates of very large wolframite crystals weighing 235 lbs. and 157 lbs. are said to have been found at the stockwork deposit, and similar groups of crystals have been obtained at the Lunar Block (the specimen in the Rhodesia Museum weighing 172 lbs. coming from here). Pieces of wolframite weighing up to 8 lbs. are not uncommon, and groups of pale pinkish scheelite crystals measuring 3 or 4 inches are to be found. The two tungsten minerals are commonly intergrown; but in spite of this and of the fact that scheelite, containing, as it frequently does, several per cent more tungstic oxide than wolframite, may be worth several pounds sterling per ton more than the wolframite, it was found that the scheelite was neglected by the workers—in fact, considerable trouble was taken by them to separate it from the wolframite and reject it.

Scheelite is a mineral very easily recognised, and the natives engaged in panning the concentrate should be taught to know it. Although it is not unlike quartz so far as colour is concerned, being white, pinkish, or yellowish, its characteristic greasy lustre, softness (it is easily scratched by the knife or by quartz), and heaviness are properties which differentiate it sufficiently from any of the minerals with which it is associated. If boiled in dilute hydrochloric acid it becomes coated with bright yellow powder soluble in alkali.

Among the dark minerals got in the concentrate, magnetite may be recognised (and separated) by the magnet, and limonite by being in brown cubes. Coarse and moderately fine wolframite is easily distinguished from the other black minerals by its greater specific gravity and chocolate-brown streak; it breaks into flat slabby pieces with lamellar structure owing to the presence of a single perfect cleavage; the flat surfaces are bright and shiny (submetallic to resinous lustre) whilst the cross fractures are dull. Ilmenite, which is rather abundant in very fine round grains in the concentrate of the rubble, is difficult to distinguish from fine wolframite by simple tests, and this fact had led to the rejection of the finest concentrate.

Mineralisation.

In addition to the minerals common to greisen, the presence both in the stockwork and in the veins of galena, pyrite, pyrrhotite, and presumably gold, together with the large amount and constant presence of a kind of quartz which is indistinguishable from the ordinary vein quartz of gold deposits, suggests that the Essexvale tungsten deposits are not normal greisens, but to some degree assume the characters of the gold quartz vein type of deposit. In fact, they appear to form a connecting link between the two types. This theory is borne out by the character of the mineralisation of the country rock alongside the greisen streaks in the stockwork deposit. The rock is pyritised (pyrite and pyrrhotite), and the felspars altered to sericitic aggregates.

The Rubble.

The richer patches of rubble lie within 100 yards of the greisens on the steeper ground and within about 25 yards on the flat ground.

Tests of this rubble indicate that the yield of wolframite (the scheelite, as noted above, being rejected) varies from 2 lbs. to 8 lbs. per ton. In this estimate the occasional lumps of coarse wolframite are not included, and fine wolframite and scheelite in lumps of rock and free are also not included, since they are rejected.

In the instance of the western end of the Lunar Block reef, it was stated that early in 1916 1600 lbs. of wolframite was picked up from the surface by hand without any appliances, without even a prospecting pan, notwithstanding that the ground had been broken, turned over, and picked on at least one previous occasion.

Where the rubble is being more thoroughly tested, the ground, made up of angular quartz fragments, brown-weathered greisen and sandstone-like aplite in a matrix of red loam, is hand jigged on rocking screens, the coarse wolframite being hand-picked from the screens. The fines are concentrate in a 5-ft. rotary diamond washer, which recovers the tungsten minerals and even the fine heavy minerals. The concentrate is then panned by hand. The coarse wolframite (pieces over ½ in.) are picked by hand, and the fines repanned. Any coarse wolframite with adhering quartz is pestled and panned. The coarse and medium concentrate so obtained is remarkably clean wolframite. The finest concentrate consists of wolframite and scheelite, with a certain amount of quartz, felspar, epidote, hornblende, mica, zircon, and tourmaline, together with a trace of gold, and a fairly large quantity of ilmenite, limonite cubes, and magnetite. The finest concentrate is rejected under existing circumstances, but on a larger scale of operations concentrating tables and magnetic separators may be expected to give profitable results.—*Bulawayo Chronicle*, May 18, 1917.

PROCEEDINGS OF SOCIETIES.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, December 5, 1917.

Mr. George Embray, President, in the Chair.

A Certificate was read for the first time in favour of Mr. Tom H. McKenzie, Chemist to the Anglo-Mexican Petroleum Co., Ltd.

Certificates were read for the second time in favour of Messrs. Kendall Colin Browning, M.A.; Frederick William Edwards; John Monteath Guthrie; Frederick Thomas Nunton; Leonard Owen Newton; Ernest Walter Wright.

The following papers were read:—

"*The Valenta Number as a Discriminative Test for Oils and Fats.*" By Percival J. Fryer and Frank E. Weston, B.Sc.

The reasons for the discrepancies in the published results for the critical temperatures of dissolution of oils and fats in various solvents are examined. Precautions are suggested to ensure uniformity of the results and the preparation of a standardised solvent for testing purposes.

"*Composition of Sharps and Bran.*" By H. E. Cox, B.Sc., A.I.C.

By order of the Food Controller wheat is now milled so as to yield 10 per cent more flour than formerly, also other cereals are mixed with it. This decreases starch in the sharps and bran, and increases fibre and pentosans. Attention is drawn to differences in content of starch and pentosans in sharps and bran, and figures are given comparing the composition of present day with pre war samples.

"*Notes on Porcelain.*" By W. T. Burgess, F.I.C.

The author describes the methods which have been adopted by the Glass Research Committee of the Institute of Chemistry for the examination of chemical porcelain. A considerable number of crucibles and basins of various origin, which had been used in the experiments, were exhibited.

"*Calorimetric Estimation of Iron.*" By E. R. Dovey, A.R.C.S.

Improvements are suggested in the method of working the calorimetric estimation of iron by the sulphocyanide method.

CHEMICAL SOCIETY.

Ordinary Meeting, November 1, 1917.

Prof. W. J. Pope, M.A., D.Sc., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of the following Fellows:—Arthur Joseph Brearley (killed in action), Bertram Howard Buttle (died of wounds), James Hector Barnes, William Thirlwall Bayne, Clayton Beadle, Oliver Statham Douse, John Joseph Eastick, Ernest George Hill, George Thomas Holloway, Rufus Daniell Pullar, William Henry Symons, Walter Arthur Voss, John Williams.

Messrs. F. G. W. Knapman, H. M. Langton, N. K. Smith, and P. Williams were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of William Gordon Adam, B.A., Product Works, Beckton, Essex; Jack Reginald Hanloss Bartlett, S. West 12, Gretna; Albert John Bishop, B.Sc., Cotswold, Bloomfield Road, Darlington; Elon Bond, B.Sc., care of Dominion Laboratory, Wellington, N.Z.; Fred Bridge, A.R.C.S., 39, Lyndhurst Road, Higham Park, Chingford, E. 4; Ranald Brightman, M.Sc., 23, Woolwich Road, Belvedere; Robert Lidwill Brown, A.R.C.S.I., 69, Paulet Road, Camberwell, S.E. 5; Arthur Calvert, 68, Belvoir Street, Princes Avenue, Hull; George William Chester, 3rd Canadian Infantry Brigade, B.E.F., France; Edward de Wykersley Swyft Colver, D.Met., Brooklands, Osgathorpe, Sheffield; John Don, M.A., B.Sc., Gardenrose, Maybole; Vernon Edge, B.Sc., 24, Chester Road, Watford, Herts; Charles Alfred Edwards, D.Sc., The University, Manchester; Herbert Wilfrid Ehrhardt, M.A., B Sc., 409, Gillott Road, Edgbaston, Birmingham; George Herbert Frank, 162, Woodsley Road, Leeds; Harold Hollings, M.Sc., 1, Northwood Road, Forest Hill, S.E. 23; John Gordon Hume, 1, Coleherne Terrace, Earl's Court, S.W. 5; George Henry Johnson, 101, Southampton Road, Northampton; James Ivor Morgan Jones, B Sc., 6, Coronation Villas, Faversham; Benedict Trembath Kitto, 26, Lancaster Road, Stroud Green, N. 4; Jacob Longman, B.A., 19, George Road, Erdington, Birmingham; Thomas Henry Mallagh, 37, Westwell Road, Streatham Common, S.W.; Edward Bradford Maxted, Ph.D., B.Sc., 63, Highgate Road, Walsall; Robert Binnie Pettigrew, M.A., 8, Hanover Road, Plumstead, S.E. 18; Alfred Arnold Pierce, 60, Drumbeck Road, Eltham; Constant Nicolas Polychronis, M.Sc., Municipal School of Technology, Manchester; Humphrey Rivaz Raikes, B.A., R.F.C., Goudhurst, Kent; Alfred Arthur Roberts, Carlton House, Yate, Bristol: Harold Salt, 37, Royal Park Avenue, Leeds; Gerald Creagh Scully, M.A., 19, Mancott Royal, Hawarden, Chester; Alfred Thomas Stanley Sissons, B.Sc., 16, Victory Avenue, Gretna; James Carter Spensley, M.A., care of Standard Bank of S. Africa, 10, Clement's Lane, E.C. 4; Henry Stephen, M.Sc., 1, Portman Street, Whalley Range, Manchester; Disney Younger Watt, Army and Navy Club, Pall Mall, S.W. 1; Albert Francis Wenger, Victoria House, London Road, Newcastle, Staffs.; David Emrys Williams, B.Sc., Uwch-y-don, Elkington Road, Burry Port; Ernest Perry Bradley Wilson, 1, Rockcliffe Terrace, Carlin How, Yorks; Frederick Charles Wond, B.Sc., 119, Latham Road, East Ham, E.6; Joseph Harry Wood, Campdene, Victoria Road, Wednesbury.

Ordinary Meeting, November 15, 1917.

Prof. W. J. Pope, M.A., D.Sc., F.R.S., President, in the Chair.

Reference was made by the President to the loss sustained by the Society, through death, of the following Fellows:—John Maxwell Heron and Herbert King.

It was announced that the President and Council had forwarded on behalf of the Society hearty congratulations to Prof. Hoogewerff on the attainment of his seventieth birthday.

Certificates were read for the first time in favour of Charles Frederick Lee Barber, 12, Queen's Terrace, Otley, Yorks.; John Boothman, Oak Villas, Whitley Bridge, S.O., Yorks.; Harry Dugald Keith Drew, B.Sc., 94, Cambridge Street, Warwick Square, S.W.; Frederick William Edwards, 283, Friern Road, Dulwich, S.E. 22; Frederick William Emerson, 179, Burton Road, West Didsbury, Manchester; Charles Henry Fielding, Minerva, College Road, Cork; Thomas Williamson Kirkwood, B.Sc., Brooklyn, Guildford Road, Farnborough, Hants; John Richard Morgan, B.Sc., 8, Heathcote Close, Ash Common, Surrey; George Johnson Twine, Staff Quarters, Sark Bridge, Gretna.

Certificates have been authorised by the Council in favour of Sarat Chandra Chatterjee, Cotton College, Gauhati, Assam; Ukendra Nath Rai Chowdhuri, Rajshahi Hospital, Rajshahi, Bengal; Shinjiro Sato, M.Sc., Oka-Honcho Street, Tokushima, Japan; George Spurge, care of Dalgety and Co., Sydney, N.S.W.

The President then closed the business of the Ordinary Scientific Meeting and declared the Informal Meeting open.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Isotropes and Radio-active Elements.—A correspondent enquires if there are any books published dealing with the following subjects:—(1) Isotropes; (2) the rate of disintegration of products of the radio-active elements.

MEETINGS FOR THE WEEK

Monday, 17th.—Royal Society of Arts, 4.30. (Cantor Lecture). "Progress in the Metallurgy of Copper," by Prof. H. C. H. Carpenter.

— Biochemical Society, 5.30. (In the Lister Institute, Chelsea, S.W.)

Tuesday, 18th.—Institution of Petroleum Technologists, 8. "The Prospective Oilfields of Barbados," by E. H. Cunningham Craig.

Wednesday, 19th.—Royal Society of Arts, 4.30. "The Cold Storage Industry," by Prof. J. Wemyss Anderson.

— Microscopical, 8. "Cytology and Genetics," by Prof. W. Bateson.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.
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THE CHEMICAL NEWS

Vol. CXVI., No. 3030.

HE IDENTIFICATION AND ESTIMATION OF ZINC IN WATER.

Part II.

By ROBERT MELDRUM.

The Colorimetric Ferrocyanide Process.

The author has discussed at length (Chem. News, cxvi., 271) a colorimetric ammonium sulphide process for the detection and estimation of zinc in water, and has shown 1 in 100,000 may be so detected and determined without previous concentration of the water. But a more sensitive reagent than this is required when a large number of samples very low in zinc contents have to be examined. Though the colorimetric ferrocyanide process was first applied by Snyder in 1878 for the detection and estimation of zinc in water its use since then does not appear to have become very general. This is no doubt due to the process not being well known, or to variable and uncertain results obtained in working the method. Its apparent deficiency in sensitiveness, and its failure to detect the metal in water when present only in traces, are other reasons for considering the process a very doubtful one. There can be no doubt that there is some justification for all this, as has been brought to light during this investigation. The process has been examined in detail by the author, who has also applied it to the detection and estimation of zinc in a large number of samples, and can with confidence recommend it if applied within its limitations, for yielding fairly accurate and rapid results. By its means 1 part Zn in one million may be identified and estimated.

Standard Zinc Solutions.

This may be prepared from pure metallic zinc, free Pb, and Fe, by dissolving 1 grm. in dilute HCl and evaporate to small bulk, dilute, and filter and make up to 1000 cc. Recently ignited pure ZnO, obtained by ignition of the carbonate or oxalate, may also be used, adjusted 1 grm. Zn per litre, or 0·001 cc. From this a weaker standard is prepared, containing 0·1 grm. Zn per 1000 cc. by dilution with distilled water. In each case it is important that the distilled water be filtered to ensure the absence of all traces of suspended matter and cloudiness. Both solutions when prepared ought to be clear, bright, and sparkling, and before being used ought to be well shaken up and examined for suspended matter, and if present must be refiltered before using. Both solutions must be maintained slightly acid. As all standard solutions of salts have a tendency to concentrate around the stopper by creeping and evaporation, it is best after extraction of stopper to withdraw the desired quantity by means of a pipette, especially when using the weaker solution.

Ferrocyanide Solution.

This solution ought not to be more than eight hours old and containing 1 per cent of the pure salt. When prepared it ought to be clear and bright and free from cloudiness, otherwise it must be filtered. 100 cc. is sufficient to prepare at any time.

Acid Solution.

A 20 per cent solution strong hydrochloric in distilled water. The acid must not contain more than traces of iron or strike a very faint red with sulphocyanide.

Apparatus.

For this class of work two 1 cc. pipettes are required for the acid and ferrocyanide solutions; also a 5 cc. pipette, each cc. being divided into tenths, for measuring out the standard solutions. Three or four stoppered test mixers of 100 cc. capacity divided into 10 cc.'s are also required, but Nessler tubes, or graduated cylinders, may also be used. The test mixers have the great advantage that efficient mixing is more efficient and less troublesome when open glasses are used. They are also much cleaner and do away with a series of glass plunger mixers, and the risk of these becoming contaminated by continual removal from the solution. Whatever the kind of tube or cylinder used these ought to have the same uniform bore or height and be of the best colourless glass. The glasses must not differ in tint, or if so this will be troublesome. Of course it is understood that no glass used in this test ought to contain zinc. This applies more particularly to the bottles in which the standard solutions are kept.

Observations.

In observing the intensity of opalescence or milkiness there is required a *dead black* tray or board, a sheet of paper or cardboard, about 12×9 inches, or larger, also a strip of black cardboard about 3×6 inches. The observations are best conducted near a window with subdued daylight. In the presence of direct sunlight a sheet of tissue paper placed in the window will subdue the light or any strong reflections. With electric and gas light the observations are more difficult and uncertain, and require careful adjustment. As the intensity of opalescence is observed in a horizontal direction right through the tube and not down the tube in the usual way, it is best to take a long line of vision 6, 7, or 8 feet off. The opalescence is best observed by looking down on the tube about 8 feet away at an angle of about 20°, and moving to left and right, to and fro, to obtain the best position and angle. A few minutes practice will soon decide this. A close range view of the colour is very well observed by holding the piece of black cardboard about 4 inches behind the tubes at a slight angle. Unless close attention is given to the observation traces of opalescence will escape attention; especially will this be so when the zinc is only present to the extent of 1 in a million.

Blank Experiment.

It is necessary to make a blank experiment during any series of tests as to the freedom of the vessels and reagents from zinc and iron. This is done by filling the test mixer with 100 cc. distilled water, or tap water, and adding 1 cc. of the acid, and well mixing by shaking and allowing to rest for a few moments, and thence adding 1 cc. of the ferrocyanide. If no trace of cloudiness or opalescence appears in twenty minutes, or no decided blue colour due to iron, or brownish colour due to copper the glasses, water, and reagents may be considered satisfactory. The next step is to add to this 1 cc. of the stronger standard, or 10 cc. of the weaker standard, and in ten minutes observe if a bluish colour develops, or if the resulting opalescence from the zinc ferrocyanide is of a bluish tinge. If of a milky white opalescence the trial may be considered satisfactory. Absolutely chemically pure standards, acid, ferrocyanide, and distilled water when free from the most minute traces of iron, or iron free, develop with the ferrocyanide a pure milky white opalescence, which condition can hardly ever be obtained in ordinary analytical work. Therefore the standards, and reagents, or water will always contain sufficient iron to give the zinc ferrocyanide a very faint bluish white appearance, the presence of which is really an advantage, as it more closely approximates the tint of the zinc ferrocyanide thrown down by the average water sample. A blank experiment also ought to be made with the laboratory tap water and compared with that of the distilled, the same amount of zinc being added in each case, as it may be necessary to use tap water instead of distilled for the standard.

The Sample to be Tested.

This must be well shaken up and the bottle carefully examined for suspended matter, cloudiness, or opalescence.

Particularly the bottom of the bottle must be examined for any adhering deposit which has settled out and attached itself to the bottom. If found this will require to be removed by means of a long glass rod with a piece of rubber tubing attached to the end, and the detached deposit mixed up with the water. 100 cc. of the water is treated with 1 cc. of the acid, and filtered through a small paper if the acid treated water still remains cloudy. 100 cc. is placed in the test mixer and 1 cc. of the ferrocyanide added. If no trace of opalescence or cloudiness appears the sample is free from zinc up to 1 part per million. If zinc is present the degree of opalescence is matched by a standard solution of zinc in tap water, which will give total zinc present in solution and suspension. To determine the soluble zinc it is only necessary to filter 100 cc. into the test mixer, treat with acid, thence with ferrocyanide, and estimate degree of opalescence. The results, therefore, are expressed as—(1) Zinc in solution; (2) Zinc in suspension; (3) Total zinc.

It may be taken for granted that a water which contains zinc in solution, and also contains matter in suspension or as a deposit, will also contain zinc in suspension. In many cases the greater part of the metal will be in suspension and very little in solution. In zinc contaminated waters the suspended matter exists in so fine a state of division, and also in the colloid state, that filtration is not effective on clarifying. Nor will the suspended zinc, when in this condition, settle within several days. Under these conditions the bottom, as well as the sides of the bottle containing the sample, become coated with a fine adhering film of the zinc deposit. It is therefore necessary to test the sides of the bottle for this film by rubbing a small area with the glass rod and rubber, and examining in a good light. If such deposit has taken place this will necessitate the filtration of the whole of the sample. Washing out the bottle with 50 cc. distilled water containing 1 cc. HCl, which may be used for dissolving the residue in filter-paper. These washings and filtrate may be made up to 200 or 300 cc. and the zinc determined in same. In many cases this will be the only method available, as some contaminated waters contain a heavy sandy sediment which settles rapidly and also adheres to sides of bottle. The estimation of zinc in water is practically valueless unless the water deposit and suspended matters are given due attention. In one particular instance the author examined a sample of water which contained 0·25 grm. of a heavy and fine deposit at bottom of Winchester quart, which consisted almost entirely of zinc carbonate.

However, in the majority of cases it is sufficient to treat 100 or 200 cc. of the sample after well shaking with 1 cc. or 2 cc. of the 20 per cent HCl, and use this for the determination of the total zinc after passing through a filter-paper. It will often save a great deal of trouble and tend to more accurate results if a sample of the water is procured previous to coming in contact with any galvanised or zinc water system. In very important cases this is a necessity, especially when the presence of the metal is known.

The Estimation.

100 cc. of the sample is placed in test mixer and acidified with 1 cc. 20 per cent HCl, if not already acidified, and 1 cc. of 1 per cent potassium ferrocyanide added. After addition of acid must be well shaken and allowed to rest for a minute previous to adding the ferrocyanide. The whole must again be well shaken, and allowed to stand for at most twenty minutes, or until an opalescence appears. The first appearance of opalescence is best observed by comparison with another test mixer filled either with distilled or tap-water only, which may be permanently retained on the black tray. Into another test mixer is placed 100 cc. of the sample which has not been in contact with a zinc coated system, or which does not react to the ferrocyanide. Distilled water for this purpose is not so suitable as the original zinc-free water. This portion is also treated with the 1 cc. acid, and 1 cc. of the zinc solution added containing 0·001 Zn per cc., and well shaken, and allowed to stand till opalescence appears. A comparison is made with the sample. If not strong enough more zinc solution is added and allowed to stand, and so on till an approximate match is made. After addition of the first cc. of zinc, if too strong colour results, abstract 20 cc., 30 cc., or 50 cc. as required, and make up with the zinc-free water. When an approximate match has been arrived at, reject the contents of test mixer and take another 100 cc. of the zinc-free sample, treat with acid, and add exactly the amount of zinc solution required in the former experiment, add ferrocyanide, and compare opalescence in ten minutes. If too weak add more zinc to standard; if too strong abstract 10 cc. or 15 cc. as the case may be, and again make up with the water, and make final comparison of intensity of opalescence in fifteen minutes. If the estimation is carried out in this manner equal quantities of zinc produce equal intensities in opalescence, but such will not hold good if distilled water is used as the standard. In this case the results are 50 to 100 per cent too high according to the character of the water being used. As natural waters vary in their colour, iron contents, alumina, silica, and saline matter in general, these also have a variable action on the zinc ferrocyanide, causing an increased opalescence according to the amount present.

Therefore when a sample of the water free from zinc is not available it is necessary to know the hardness of the water, its alkalinity, its chloride and sulphate contents, also the iron and alumina, or a general analysis of its mineral constituents, so that an artificial water may be prepared containing the predominating saline matter present, to be used as a standard. Standard calcium chloride solution, equivalent to 0·2 grm. $CaCO_3$ per litre, as used for standardising soap solution, is useful in this respect for giving to distilled water a temporary hardness equal to that of the sample, and so on with the main saline constituents. This is where the ferrocyanide colorimetric process has its limitations. As a qualitative test it is certain, accurate, and sensitive up to one part per million, also as a quantitative test when a similar zinc-free water is available as a standard. Even with these limitations the process is a most useful one in many ways.

Dec. 9, 1917.

THE FRUIT OF THE *ASPARAGUS OFFICINALIS*, L.

By N. E. HEHNER.

THE fruit of the *Asparagus officinalis*, L., was of the variety that is most commonly cultivated and with which everyone is more or less familiar. The berries seemed quite ripe, having a deep red colour, and were spherical in shape, resembling currants in size. Their average diameter was from 7 to 8 mm., and average weight, when dried, 0·1398 grm. The fruit had a very bitter and unpleasant taste when dried. There was a small amount of red pithy substance between the hulls and seeds. Each berry had from three to five small black seeds, having the shape of coffee berries, and fitted together so as to form a small ball in the centre of the berry. The seeds were very hard and difficult either to crush in an agate mortar or grind in a coffee grinder. When the fruit was ashed, only one distinct odour was noticed, and that was of burning leaves. Heat was applied to the berries until the ash became a white colour. Most of the ash came from the seeds, the hulls burning up to almost nothing. The fruit for this analysis was gathered in the vicinity of Mount Vernon, Iowa. There was about 700 grms. of the fruit available for the analysis.

Sugars.

200 grms. of the fruit was placed in a large flask, fitted with an inverted condenser apparatus. It was then treated daily with 95 per cent alcohol on a water-bath for about forty days. The excess alcohol was distilled off each time

and an extremely dark red solution remained. Finally the extraction appeared almost colourless and very little sugar remained after this treatment. Water was then substituted for the alcohol, to make sure that all the sugars would be taken out in the process. The method of extraction was the same as in the case of alcohol, and treated for ten days. At the beginning of this stage the solution was very dark red in colour; but after several changes of water the solution became colourless. This water extraction took out the last trace of sugar that the alcohol had failed to remove. The solution was tested from time to time with Fehling's solution to indicate the presence of sugars. Neither one of the solutions reacted upon litmus paper. After the two extractions were mixed together and allowed to stand. there was an odour of cider, showing that some of the sugars were fermenting. This fermentation was very small and would be extremely difficult to calculate and so was not determined. The berries, while under the alcoholic treatment, seemed to be affected but very little in appearance, but after water was added they became somewhat mushy. Much more sediment came down in the water extraction than in the alcoholic extraction.

The percentage of sugar was determined by means of Fehling's solution of such strength that 10 cm. corresponded to 0·05 grm. of sugar. One centimetre of the extraction was then taken, diluted to 50 cc. with distilled water, heated to boiling and titrated with Fehling's solution. The end of the reaction was very hard to ascertain. but was done in the following manner:—After a small amount of the Fehling's solution was added, the solution was filtered and the process continued until it turned from a straw colour to a pale blue.

It was very essential that the sugar extraction was kept at boiling tempereture as better results were obtained with a hot solution than even with a warm solution. The amount of sugar present was 36·12 per cent.

The residue of the sugar solution was evaporated to dryness, water added, and it was purified with bone black. The residue had the odour of scorched sorghum and a slightly bitter taste, somewhat the same as that of the original berry. The residue was a black, thick, sticky, jelly mass. The test, made by phenylhydrazine, for the kind of sugars present seemed to show fructose. The tests for the other sugars were unsatisfactory.

200 grms. of berries were taken at first and after the sugar extractions weighed 113 grms. This showed a loss in weight of 43·5 per cent. Most of the berries still maintained their shape and were a little lighter in colour than before the treatment.

Ash.

Four different portions of berries were ashed in a small platinum dish. From the first portion, silica, iron, aluminium, calcium, and magnesium were determined; from the second portion, sodium and potassium, according to a slight modification of the J. Lawrence Smith method; from the third portion, sulphates, by means of barium chloride; and from the fourth portion, phosphates, by means of ammonium molybdate. The average percentage of ash in the berries was 3·5 per cent.

First portion—

SO_2 and insoluble residue.	2·53 per cent of the ash.
A_2O_3	0·98 " "
Fe_2O_3	2·53 " "
CaO	3·52 " "
MgO	6·09 " "
Weight of berries taken ..	2·3651 grms.
Weight of ash	0·0710 "

Second portion—

K_2O	5·35 per cent of the ash.
Na_2O	8·73 " "
Weight of berries taken ..	2·4403 grms.
Weight of ash	0·0946 "

Third portion—

SO_3	7·91 per cent of the ash.
Weight of berries taken ..	2·2666 grms.
Weight of ash	0·0759 "

Fourth portion—

P_2O_5	25·01 per cent of the ash.
Weight of berries taken ..	2·7176 grms.
Weight of ash	0·0964 "

The fourth portion was determined by dissolving the ash in nitric acid and filtering, treating the filtrate with ammonium molybdate.

The carbon dioxide that was in the ash was not determined because it was difficult to remove the ash from the dish without the aid of acids. There seemed quite a large amount of carbon dioxide present.

A portion of the berries, after the sugar and oil extractions, was ashed and the result was 1·01 per cent ash as compared with 3·5 per cent in the original fruit. This showed a loss in ash of 2·5 per cent during the extractions. It also took a much larger bulk of fruit to weigh a certain amount than before. It required a much shorter time to ash this portion and the same characteristic odour of burning leaves was present.

Oils.

The dried berries from the sugar extractions were used in this extraction. An attempt was made to grind the berries in a coffee mill, but on account of the hardness of the seeds it was not a success. The berries were then treated in the same way as for the sugar extraction, only ether was substituted for alcohol and water. Daily extractions were taken for about three weeks when the extracted liquid was quite free from any coloration whatever. At the end of three weeks the ether was distilled and the oil remained. Some time was required to evaporate all the ether from the oil. It finally resulted in a semi solid mass, having the colour of a good quality of vaseline and the odour of castor oil. Not enough of the oil was obtained to determine the boiling point. At low temperatures it became fairly hard.

Two attempts were made in determining the specifie gravity. The first result was 0·9005, and the second 0·8950. These two were taken about two weeks apart, which showed that either the ether had not entirely evaporated in the first result or else it had dried somewhat in the second result. The percentage of oil was 1·08.

Only only one attempt at saponifying the oils was made, on account of the small amount obtained. A N/10 caustic potash solution was made, using absolute alcohol instead of water. A definite amount of this with a definite amount of the oil was placed in a flask fitted with an inverted condenser. After heating for about twenty hours the oil seemed to be saponified. 2·5 grms. of the oil was taken and the saponification equivalent was found to be 178·57. This equivalent is between valerin and laurin, which includes such oils as cocoanut, whale, dolphin, and palmnut.

Proteins.

Albomen was found only in small quantities by taking a water solution of the berries and heating with nitric acid. The acid solution turned yellow in the presence of albumen and orange-red when made alkaline with ammonia. The fruit when heated gave off fumes which had no effect upon either red or blue litmus paper.

In the nitrogen determination, the Gunning method was followed. 0·5 grm. of the berries was taken, and this gave 0·00784 grm. of nitrogen, which equals 1·56 per cent.

Because of the small amount of albumen, the test for sulphur in the albumen was not satisfactory.

Acids.

Of the common acids only two seemed to be present. A large amount of malic acid along with a trace of citric acid was found to be present, while tartaric and oxalic acids were absent.

I wish to express my appreciation and thanks for the assistance of Dr. Nicholas Knight in this analysis.

Cornell College, Mount Vernon, Iowa,
November 12, 1917.

A CONTRIBUTION TO THE THEORY OF SOLUTION.*

By E. J. HARTUNG, B.Sc.

(Continued from p. 286).

Aniline and Ether.

The experimental results for this liquid-pair are given in the following tables:—

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* A Paper read before the Faraday Society.

Table III.—*Contractions at 20°.*

M.	N.	D.	V	Δ_v.
0	0	1·02197	91·07	0
14·54	0·1761	0·97322	92·19	1·13
30·78	0·3584	0·92101	93 66	2·00
44·45	9·5013	0 87845	95·11	2·38
54·20	0·5979	0 84874	96 28	2·46
55 85	0·6138	0·84373	96·49	2·44
62·19	0 6738	0·82466	97·34	2·37
71·76	0·7615	0 79606	98·75	2·08
80·38	0·8373	0·77054	100·15	1·65
100	1·0000	0·71308	103·90	0

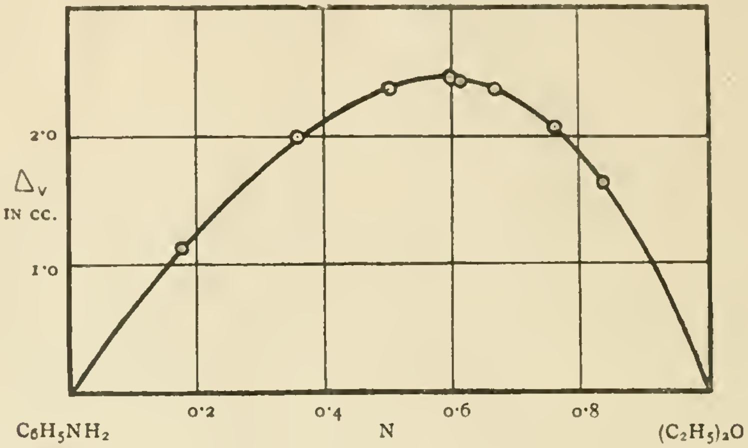

Fig. 5.

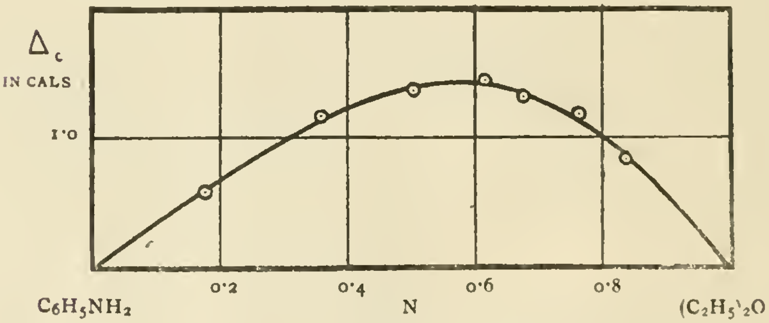

Fig. 6.

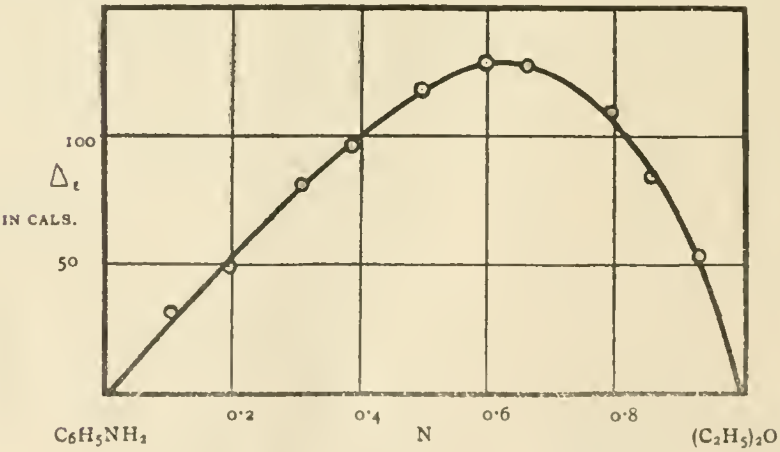

Fig. 7.

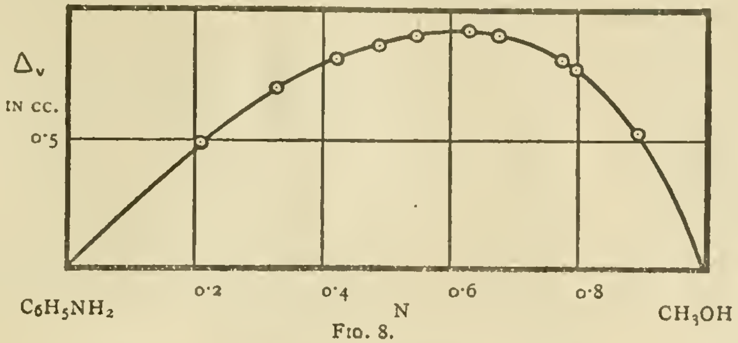

Fig. 8.

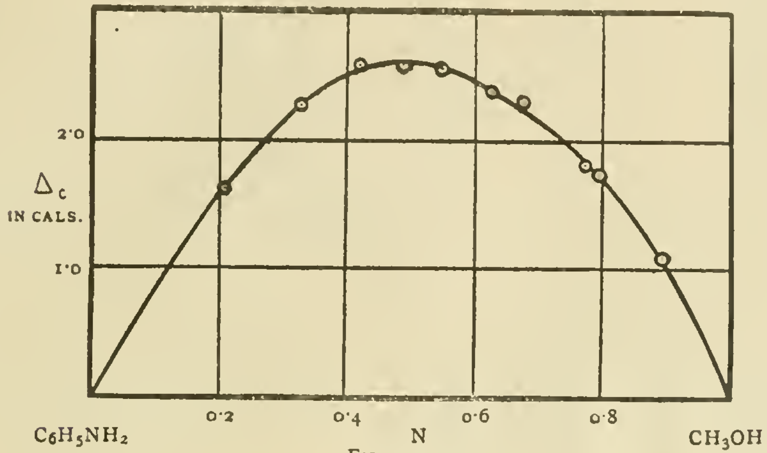

Fig. 9.

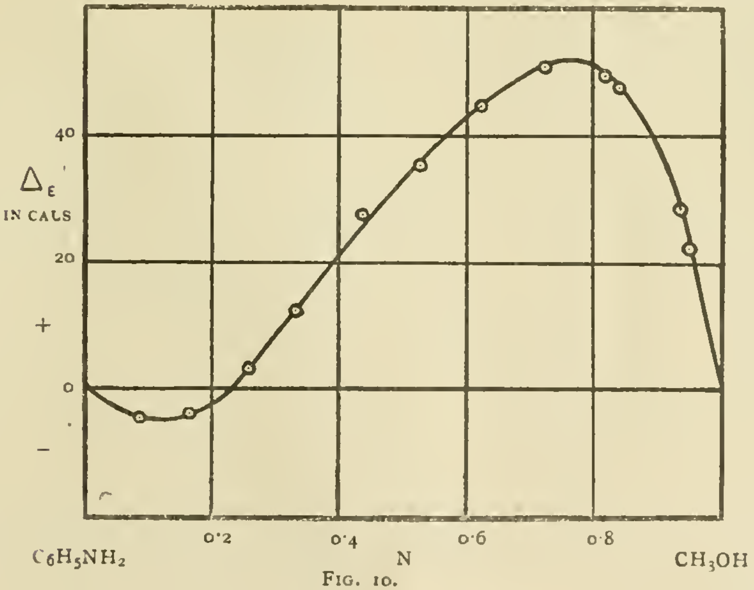

Fig. 10.

The curves drawn from these three sets of results are given in Figs. 5, 6, and 7 respectively. The departure of each property from the mixture law is strongly marked. The curves of contraction (Fig. 5), of heat capacity deviation (Fig. 6), and of heat evolution (Fig. 7) are similar to each other in general form, but they are not symmetrical and do not reach a maximum at $N = 0\cdot5$, but rather in the neighbourhood of $N = 0\cdot6$. Also the gradients at the ends of all the curves have definite values. Hence, here again no single solvate supposition will explain the experimental facts, and we are forced to assume the presence of two or more solvates.

TABLE IV.—*Heat Capacity at 20°.*

M.	N.	S.	C.	Δ_c
0	0	0·472	43·94	0
14·54	0·1761	0·490	43·84	0·59
30·78	0·3584	0·507	43·72	1·18
44·45	0·5013	0·520	43·36	1·39
55·85	0·6138	0·528	42·90	1·47
62·19	0·6738	0·531	42·64	1·34
71·76	0·7615	0·537	42·15	1·20
80·38	0·8373	0·535	41·50	0·84
100	1·0000	0·540	40·02	0

TABLE V.—*Heat Change at 20° (Positive).*

M.	N.	E.	Δ_E.
8·38	0·1031	33·82	30·82
16·02	0·1933	54·94	49·12
25·98	0·3060	92·50	80·72
33·10	0·3833	112·98	96·93
43·80	0·4947	142·07	118·88
54·02	0·5961	158·53	129·60
62·88	0·6802	160·51	128·64
75·27	0·7927	141·06	110·05
82·76	0·8579	110·01	84·48
91·30	0·9294	71·31	53·79

Aniline and Methyl Alcohol.

The experimental results for this liquid-pair are given in the following tables:—

TABLE VI.—*Contractions at 25°.*

M.	N.	D.	V.	Δ_v.
0	0	1·01744	91·47	0
8·21	0·2063	0·99964	80·52	0·49
14·22	0·3252	0·98602	74·26	0·70
19·95	0·4199	0·97271	69·34	0·82
24·58	0·4863	0·96193	65·90	0·87
29·40	0·5474	0·95056	62·75	0·91
36·62	0·6267	0·93360	58·72	0·93
42·00	0·6777	0·92097	56·13	0·91
54·10	0·7740	0·89283	51·33	0·82
57·71	0·7986	0·88416	50·13	0·78
74·71	0·8956	0·84489	45·45	0·53
100	1·0000	0·78740	40·68	0

TABLE VII.—*Heat Capacity at 25°.*

M.	N.	S.	C.	Δ_c.
0	0	0·484	45·02	0
8·21	0·2063	0·512	41·35	1·62
14·22	0·3252	0·534	38·95	2·27
19·95	0·4199	0·547	36·85	2·59
24·58	0·4863	0·553	35·15	2·59
29·40	0·5474	0·568	33·55	2·56
36·62	0·6267	0·571	31·35	2·39
42·00	0·6777	0·577	30·95	2·30
54·10	0·7740	0·595	27·00	1·82
57·71	0·7986	0·587	26·30	1·75
74·71	0·8956	0·601	23·15	1·09
100	1·0000	0·605	19·39	0

TABLE VIII.—*Heat Change at 25°.*

M.	N.	E.	Δ_E.
3·12	0·0855	−4·89	−4·30
6·32	0·1639	−4·59	−3·81
10·58	0·2558	+4·69	+3·63
14·48	0·3297	+17·4	+12·7
21·01	0·4359	+41·9	+27·8
27·65	0·5261	+58·2	+35·5
36·01	0·6205	+81·2	+44·8
47·30	0·7228	+104·9	+51·4
60·61	0·8172	+115·1	+49·7
64·32	0·8397	+114·7	+47·9
83·49	0·9362	+80·1	+28·8
86·42	0·9486	+63·7	+22·4

The curves drawn from these three tables are shown in Figs. 8, 9, and 10 respectively. This case is quite unsuitable for consideration from the simple solvate standpoint, since methyl alcohol is notoriously associated. In fact, a solution of aniline in methyl alcohol shows some similarity to one of ammonia in water, in that it is capable of dissolving small amounts of copper oxide, giving a green solution. The deviation curves for this mixture are, however, very interesting, although it is quite impossible to fit any simple theory to the experimental results. The contraction curve (Fig. 8) has quite a different maximum to the heat capacity deviation curve (Fig. 9), while the heat change on mixing curve (Fig. 10) is remarkable in showing both a maximum and a minimum. Qualitatively, this behaviour is easily understandable. We may suppose that two simultaneous sets of actions occur on mixing the component liquids—

(i.) Formation of one or more solvates, accompanied by heat evolution.

(ii.) Partial dissociation of the methyl alcohol, accompanied by heat absorption.

When the mixture is rich in alcohol (i.) predominates, and we have a maximum near the alcohol end of the curve. When the mixture is rich in aniline (ii.) predominates, and we have a corresponding minimum near the aniline end of the curve. A quantitative theory must be extremely difficult to apply, in consequence of our lack of knowledge of the association changes which take place when methyl alcohol is mixed with its partner.

(To be continued).

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART II.—LIQUIDS.

By IRVING LANGMUIR

(Continued from p. 288).

EXTREMELY interesting effects are observed when very small quantities of hydrochloric or sulphuric acids are added to the water. Figs. 10, 11, and 12 illustrate the curves obtained with water at 16° containing 0·1 per cent of hydrochloric acid (0·028 N). The points marked S indicate where the films become solid. For comparison the curve (Fig. 8) normally obtained in the absence of the mineral acid is shown as a dotted line in each figure. It is interesting to note that the first kinks in the curve (marked H in Figs. 10, 11, and 12) occur at points which lie approximately on the normal curve (dotted line).

In carrying out these measurements the weights were placed on the pan of the balance and then the paper strip A (Fig. 6) was moved along until the movable strip B came to rest under the point J. When the point H on the curve was reached it was found that the strip B would not remain permanently under the point J but would very slowly move to the left. In order to keep the strip under the point it was necessary continually to advance the strip A. At first this shrinking of the film was slow (about 10 per cent in thirty seconds), but as the area decreased the shrinking became more and more rapid. The last third of the line HV (Figs. 10 and 11) was passed over in a few seconds. These results suggest that the transformation which occurs in the film is of the nature of a change in phase and that the rate of change depends upon the number of nuclei of the new phase present at any time. These phenomena were further studied by taking weights off the pan after the film had begun to shrink, that is, after the point H (Fig. 10) has been passed. By then putting back the weights one by one it was possible to observe the curve RV, which forms a lower extension of the curve VF.

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* From the *Journal of the American Chemical Society* xxxix., No. 9.

The force per cm. which must be applied to cause shrinking to begin (at H) is somewhat variable and depends to a considerable extent upon the rapidity with which the readings are taken. For palmitic acid the ordinates of the kink H have been found to vary between 26 and 34 dynes per cm., the smaller force corresponding to the slower taking of the readings.

Experiments were undertaken at several temperatures and with many different strengths of hydrochloric acid. With palmitic acid the curves obtained at 4° were the same as those at 16°, except that the ordinate of the point H was somewhat greater, about 30—38 dynes per cm. With impure arachidic acid at 16° the kink H occurred at about 60 dynes per cm,, while at 35° it was observed at 48 dynes per cm.

Within wide limits the strength of the acid had no appreciable effect on the curves. About one part of HCl in a million of water was sufficient to cause the curve to change from that shown in Fig. 8 to that in Fig. 10, and a 10,000 fold further increase in the strength made no further change. These films are thus extraordinarily sensitive to very small quantities of acid.

It was found that sulphuric acid gave exactly the same effect as hydrochloric acid. A small amount of hydrogen sulphide dissolved in the water gave a kink H as in Fig. 10, but the curve VF was shifted much further to the right and the point Q came further to the left. The abscissa of H was about the same as for hydrochloric acid. In another case 0·2 per cent of potassium cyanide, together with 0·01 per cent of hydrochloric acid, were added to the water. This gave a curve in which the kink H occurred at $a = 18{\cdot}6 \times {}^{-16}$ sq. cm., $F = 27$ dynes per cm., while the kink V occurred at $a = 11 \times 10^{-16}$ sq. cm. The point Q was at $a = 26 \times 10^{-16}$.

These results seem to show that as the hydrogen-ion concentration is made extremely small the curve RF shifts to the right and the point Q shifts to the left, while the kink H remains practically fixed.

Curve I (Fig. 12) was obtained with a sample of arachidic acid of doubtful purity. The film became solid just before the vertical part of the curve (below H) was reached. The sample of the acid was then fractionally distilled in high vacuum, the first and last thirds being rejected. Curve II was then obtained. In this case the film became solid at the point marked S′, which is located in a position corresponding to those observed with palmitic and stearic acids (Fig. 10 and 11).

Myristic acid on 0·1 per cent hydrochloric acid at 16° gave a curve very much like that found with palmitic acid (Fig. 10). The maximum area per molecule was, however, considerably greater, $a = 52 \times 10^{-16}$ sq. cm. The film became solid at a point corresponding to S in Fig. 10.

Cerotic acid films were not changed by the presence of hydrochloric acid; that is, the curves always resembled those of palmitic acid on pure water (Fig. 8).

With dilute solutions of salts such as the chlorides of sodium, calcium, or magnesium the curves obtained are not very greatly different from those found with distilled water (Fig. 8). The small effects which do occur with these and other salts are being made the subject of further study.

Saturated Alcohols. — Cetyl ($C_{16}H_{33}OH$), ceryl ($C_{26}H_{53}OH$), and myricyl ($C_{30}H_{61}OH$) alcohols were studied. The curve obtained for cetyl alcohol is given in Fig. 13. The maximum area per molecule a_0, is 21×10^{-16} sq. cm., which is about the same as that of the saturated acids on distilled water. The film of this substance is liquid even when compressed into a small area, and even when the water is cooled to 4°. It would seem therefore that the compression and expansion of such a film should be practically reversible instead of showing the marked hysteresis observed with the solid films of the saturated fatty acids. This, however, is by no means the case. In compressing the film, the force must be increased as shown by the curve QHU (Fig. 13). If now the weights are removed gradually no perceptible expansion of the film occurs until the point V is reached, and then the area increases as shown by the curve VR. This hysteresis loop is not greatly different from those observed with solid films yet the cetyl alcohol film is extremely mobile.

Cetyl alcohol and myricyl alcohol give solid films. The curves obtained are, however, very similar to those of cetyl alcohol except that a_0 is considerably larger. With myricyl alcohol it seems to be difficult to get consistent results, perhaps owing to the great thickness and hence stiffness or rigidity of the film. When one or two drops of the benzene solution is applied and the benzene has evaporated, it is found by sprinkling talc on the surface that the film has gathered into large cakes. When the area is decreased these cakes pack together leaving irregular spaces between them. On still further decreasing the area the cakes crush each other at their points of contact. It is therefore not surprising that the values of a_0 vary from about 20 to 31×10^{-16} sq. cm.

Within the range from 4 to 45°, temperature seems to have no important effect on the shapes of the curves obtained with these alcohols. The addition of hydrochloric acid to the water is also without apparent effect.

Saturated Esters.—Tristearine, $(C_{17}H_{35}COO)_3C_3H_5$; cetyl palmitate, $C_{15}H_{31}COOC_{16}H_{33}$; amyl stearate, $C_{17}H_{35}COOC_5H_{11}$; and ethyl palmitate, $C_{15}H_{31}COOC_2H_5$, were the esters investigated. The curve for tristearine was of the same type as that of palmitic acid (Fig. 8). The value of a_0 was 68×10^{-16} sq. cm., while the kink H occurred at $a_H = 48 \times 10^{-16}$ and $F_H = 61$ dynes per cm.

With cetyl palmitate (Fig. 14) the curves obtained at different temperatures differed greatly. At 4° and at 16° the curves closely resembled those for palmitic acid (Fig. 8), and gave values of a_0 ranging from 20·5 to 25×10^{-16} sq. cm., while a_T (see Fig. 7) was always very close to $20{\cdot}5 \times 10^{-16}$. At higher temperatures, however, the value of a_0 increased to 37×10^{-16} at 35°, 52×10^{-16} at 40°, and about 95×10^{-16} at 45°. At all temperatures the film became solid at approximately the same area of 23×10^{-16} sq. cm.

Typical results with amyl stearate are shown in Fig. 15. At 4° the film became solid at the point marked S, but at 16° and higher temperatures the film remained liquid even when greatly compressed. Between 4° and 46° the temperature had relatively little effect on the results except where the film became solid at 4°. The area per molecule a_0 averaged about 95×10^{-16} sq. cm. The curves for amyl stearate thus resemble those obtained with cetyl palmitate at the highest temperatures. One dotted curve in Fig. 15 shows the results for cetyl palmitate at 45° as taken from Fig. 14, but replotted to the same scale as that used for the amyl stearate. A second dotted curve gives for comparison the data for palmitic acid as taken from Fig. 8.

Ethyl palmitate gives a rather similar curve which is also shown in Fig. 15.

Curves obtained with cetyl palmitate and amyl stearate on water containing hydrochloric acid did not differ materially from those on pure water.

Tristearin on 0·1 per cent hydrochloric acid, on the other hand, gave a curve rather similar to that of stearic acid in Fig. 11. The value of a_0 was 108×10^{-16} sq. cm. as compared to 68×10^{-16} for tristearin on pure water. The kink H occurred at $a_H = 53 \times 10^{-16}$; $F_H = 48$. The film of tristearin on the acidulated water remained liquid until the area per molecule had been reduced to $a = 21 \times 10^{-16}$ sq. cm.

Unsaturated Acids.—Oleic, $C_{17}H_{33}COOH$; erucic, $C_{21}H_{41}COOH$; linoleic, $C_{17}H_{31}COOH$; linolenic, $C_{17}H_{29}COOH$; and ricinoleic, $C_{17}H_{32}(OH)COOH$ acids were tried. The curves for oleic, linoleic, and linolenic acids are given in Fig. 16. The data for palmitic acid (Fig. 8) is also given (as dotted curve) for comparison. Hydrochloric acid in the water produces a marked effect

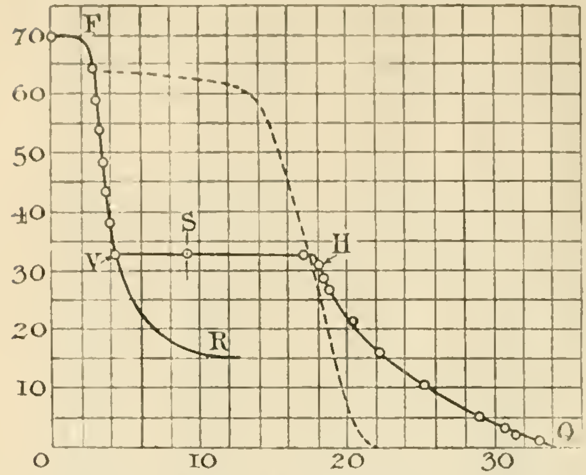


Fig. 10.—Palmitic Acid on Water containing 0·1 per cent HCl.

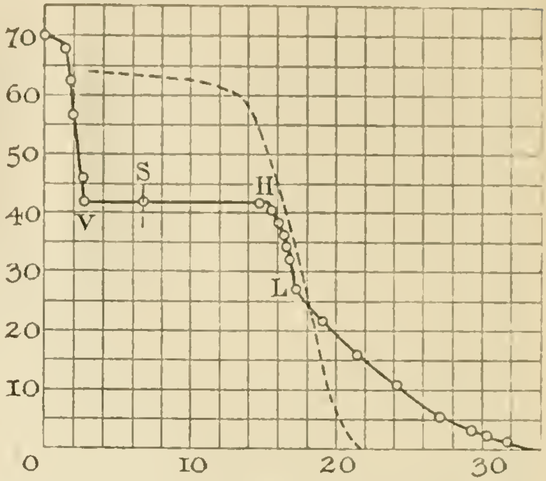


Fig. 11.—Stearic Acid on Water containing 0·1 per cent HCl.

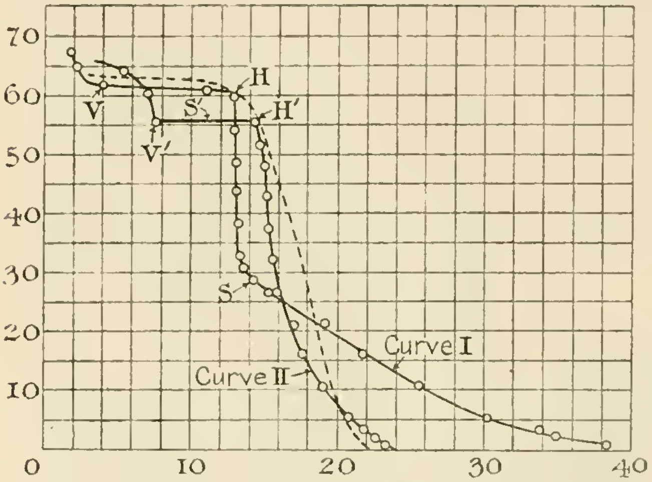


Fig. 12.—Arachidic Acid on Water containing 0·1 per cent HCl.

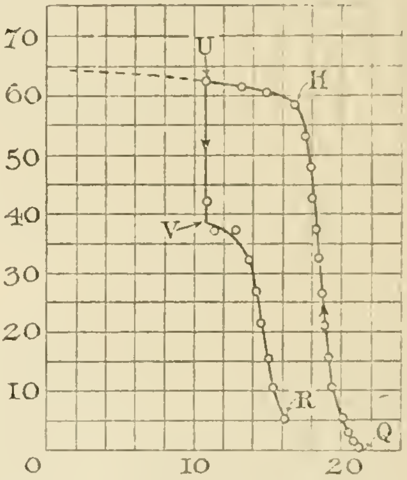


Fig. 13.—Cetyl Alcohol on Water.

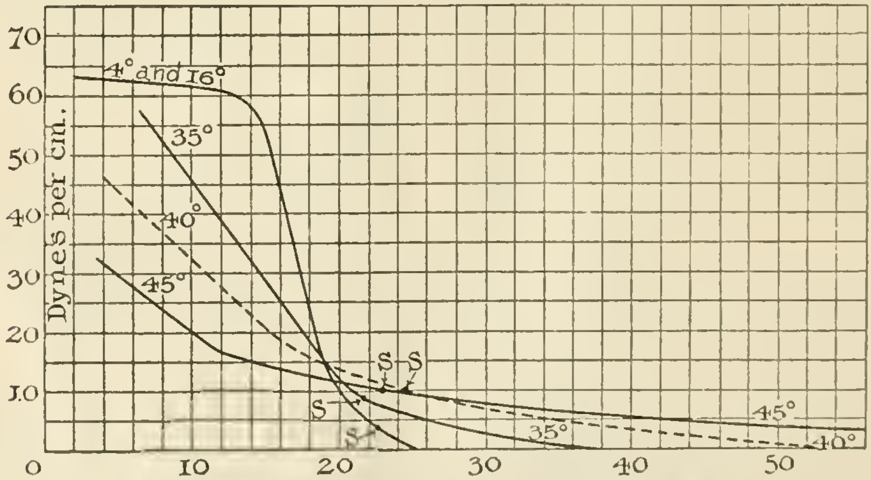
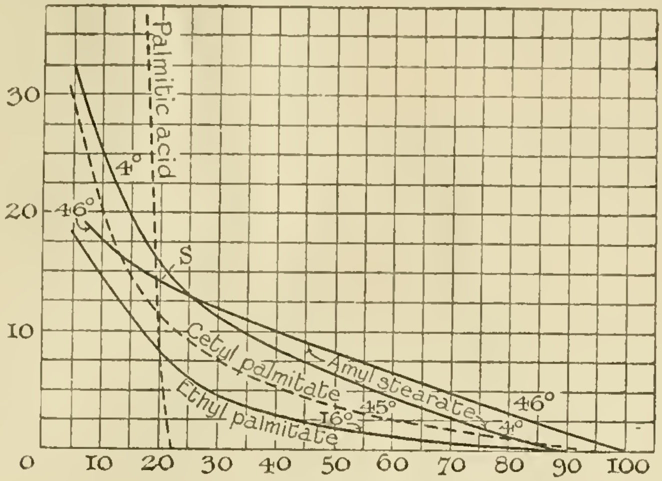


Fig 14.—Cetyl Palmitate on Water at different Temperatures.



G. 15.—Saturated Esters on Water.

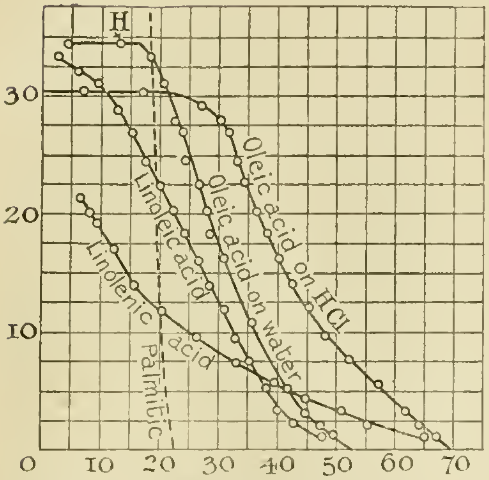


FIG. 16.—Unsaturated Acids on Water.

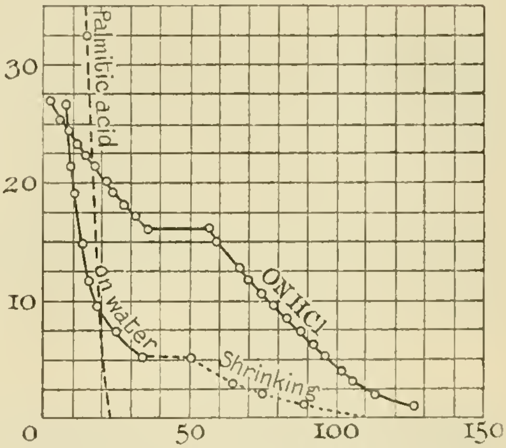


FIG. 17.—Ricinoleic Acid on Water and on Water containing 0·1 per cent HCl.

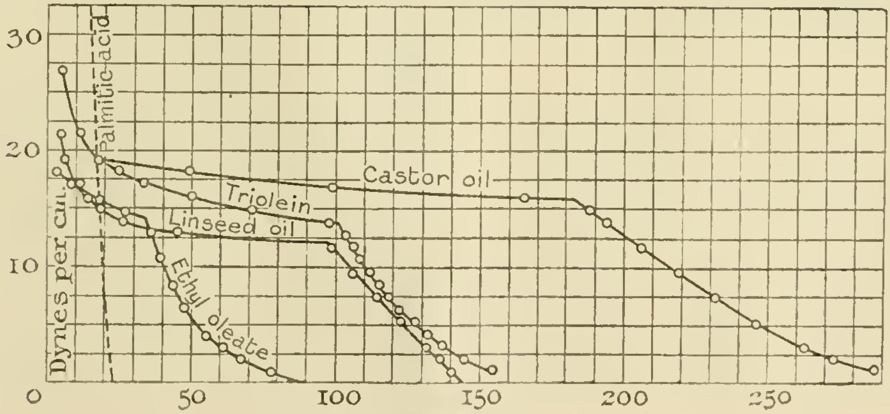


FIG. 18.—Unsaturated Esters.

on the oleic acid film, causing it to increase in area as shown in the curve.

Erucic acid gave a curve very much like that of oleic acid (Fig. 16). The co-ordinates of the important points were—

$a_0 = 44 \times 10^{-16}$ sq. cm.
$a_H = 12.6 \times 10^{-16}$. $F_H = 36$ dynes per cm.

The film remained liquid until very highly compressed.

Upon adding hydrochloric acid the curve underwent approximately the same changes that occurred with palmitic acid, giving a curve similar to Fig. 10. The co-ordinates were—

$a_0 = 82 \times 10^{-16}$ sq. cm.
$a_H = 27 \times 10^{-16}$. $F_H = 26$ dynes per cm.
$a_V = 7 \times 10^{-16}$. $a_S = 10 \times 10^{-16}$ sq. cm.

Ricinoleic acid (Fig. 17) gave remarkable results. On distilled water no constant readings could be obtained until a force of more than 4 dynes per cm. had been applied. With smaller forces the area would continually shrink, so that the curve obtained depended entirely on the rapidity with which the readings were taken. This part of the curve is indicated by a dotted line. On hydrochloric acids, as well as on various salt solutions, this tendency to shrink disappeared. The curve obtained with dilute hydrochloric acid (0·1 per cent) is given in Fig. 17. Two kinks with a horizontal part of the curve between them were observed as in the case of the saturated fatty acids (Figs. 9 and 10). These results may be complicated by the presence of impurities.

Unsaturated Alcohols.—Anhydrous cholesterol was the only substance of this class investigated. The curve obtained resembled that with oleic acid on pure water (Fig. 16). The following values of the co-ordinates for the singular point were found:—

$a_0 = 44 \times 10^{-16}$ sq. cm. $a_S = 15 \times 10^{-16}$ sq. cm.
$a_H = 11 \times 10^{-16}$ sq. cm. $F_H = 45$ dynes per cm.

The addition of hydrochloric acid to the water (0·1 per cent) caused the curve to take the general character of the curve for palmitic acid on the acid (Fig. 10). The constants were:—

$a_0 = 72 \times 10^{-16}$ sq. cm.
$a_H = 23$ to 28×10^{-16}.
$F_H = 27$ to 35 dynes per cm.
$a_S =$ about 10×10^{-16} sq. cm.
$a_V = 9 \times 10^{-16}$.

Unsaturated Esters.—Triolein, $(C_{17}H_{33}COO)_3C_3H_5$; trielaidin, $(C_{17}H_{33}COO)_3C_3H_5$; ethyl oleate, $C_{17}H_{33}COOC_2H_5$; linseed oil, $(C_{17}H_{31}COO)_3C_3H_5$; castor oil, $[C_{17}H_{32}(OH)COO]_3C_3H_5$; and many other oils were studied. Some of the results are given in Fig. 18.

The rising parts of the curve for small values of *a* may well be due to small amounts of saturated fatty acids or esters. The curve for trielaidin was practically identical with that of triolein.

(To be continued).

THE TREATMENT AND TRAINING OF CASES OF SURGICAL TUBERCULOSIS.*

By HENRY J. GAUVAIN, M.A., B.C.,
Medical Superintendent, Lord Mayor Treloar Cripples' Hospital and College, Alton, Hants.

Introduction.—Attention is directed to the extraordinarily increased interest taken in questions relating to social welfare. This is exemplified by maternity and child welfare schemes, the preservation of infant life, a Ministry of Health, better housing conditions, &c. Incidentally a great stimulus has been given to and increased interest taken in the anti tuberculosis campaign. The war has emphasised the sacredness and value of human life.

With this increased interest in social reform there are dangers into which the very energy and enthusiasm of its advocates may lead us. A conspicuous and terrible example of this is offered by the Russia of to-day. The present mood of the public may be all too successfully exploited by eager reformers. It is essential therefore that we should concentrate on those lives which experience has taught us are certain to be productive of success and benefit to those concerned. I shall therefore rigidly confine my remarks to a demonstration of principles employed in the treatment and training of patients suffering from surgical tuberculosis, which have been proved beyond doubt to be successful and economical.

Chronic disease has for too long been regarded from the purely pathological standpoint. For this both the physician and the public is to blame.

Patients suffering from a chronic disease which necessitates prolonged treatment, should not be left intellectually destitute nor debarred from such industrial training as is possible with due regard to their limitations.

This desideratum has been ever kept in mind by Sir William Treloar, whose efforts have combined compassionate philanthropy with the exercise of wisdom and common sense.

The treatment of surgical tuberculosis at Alton is essentially conservative. It has been characterised by Mr. Balfour as no longer an experiment but an assured success. Lord Moulton has said, "The methods used are of the highest interest, not only to the man of science, but also to those who rejoice to see successful results attained by stimulating rather than supplanting the efforts of nature to defend itself from disease." The patients are placed in ideal climatic conditions, have abundant access to fresh air, sunlight, good food, the affected parts kept at rest with appropriate splints and appliances; deformity is prevented, or corrected where possible, and during treatment all children above the age of five years receive education designed especially to meet their requirements, and administered by trained, certificated, and specially selected teachers. Boys remaining crippled when treatment is completed are drafted, where possible, to the College. Here they are detained for a period of three years, their education is continued, and they are instructed in a trade suited to their limitations.

An example of the value of this method of treatment and training may be cited by reference to the following case:—

"D. R. was admitted to the hospital October 25, 1908, suffering from tuberculous disease of the hip-joint with discharging infected wounds, and considerable deformity. He was ill-nourished, weakly, and cachectic, a mouth breather, and apparently mentally dull. His disease was arrested, deformity corrected, sinuses healed, tonsils and adenoids removed, and he was educated. On August 30, 1909, he was transferred to the College for training and continued treatment, and detained there for three years.

"Present condition: He now walks with hardly perceptible limp, has been passed for Military Service by a Medical Board, is employed on Government work, and is now, I am informed, earning £7 15s. weekly and overtime as Inspector of machine gun manufacture. I am told he has earned over £1000 during the last two years."

While this is an exceptional case, the results are surprisingly good as a whole. Patients after discharge are kept under observation, receive both medical and sociological advice, and are directed into such occupations as would afford them the best prospects of remunerative employment despite any physical disabilities which may persist.

Since the hospital was opened 1890 cases have been admitted, 26 have died (1·67 per cent), 1517 have been discharged with disease arrested (93 per cent).

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* Abstract of Lecture delivered at the Royal Institute of Public Health, December 12, 1917.

The mortality rate in hospital is actually lower than that of the mean annual mortality rate amongst all children of similar age in England and Wales. The ordinary mortality amongst patients sufficiently severely infected to seek institutional treatment cannot be exactly stated, but there is reason to believe it varies from between 40 and 50 per cent of those who seek relief.

In England and Wales in the years 1914 to 1916 inclusive 71,007 cases of non-pulmonary tuberculosis were notified, and 25,451 under fifteen years of age are registered as having died of this condition.

This heavy mortality could be very largely reduced. To attain this end it is suggested that treatment in such specialised hospitals as Alton should be generrally available. Children, while under treatment, should be educated, adolescents trained in a suitable trade, and adults employed or occupied. On discharge they would not only have their disease arrested but would be mentally or industrially equipped for a useful career. These patients should only be detained in general hospitals for observation and diagnosis, and should be as speedily as possible transferred to special institutions as described. General hospitals have not facilities for the specialised treatment required, their beds are properly and urgently needed for acute cases, and both patients and public would benefit if this urgently needed reform was instituted.

It is a matter of encouragement that public interest is being awakened on this subject, and all the signs are that this much needed reform will be accomplished.

The lecture was illustrated with numerous lantern slides depicting the treatment and training given at Alton for patients suffering from surgical tuberculosis.

GERMANY'S FAITH IN ELECTRICITY.

A Challenge to British Enterprise.

Coinciding with the publication of the Coal Conservation Committee's Report by the Ministry of Reconstruction, which we are officially informed is imminent, interesting discussions in Germany, of which reports have reached this country, indicate that great reliance is to be placed on intensive development of electric power as a chief agent of rapid reconstruction of industrial prosperity.

One of our most eminent consulting engineers has favoured *Electrical Industries* with the following pithy and emphatic comment on these designs of our chief enemy:—

"It is true that Germany had before the war gained enormous economic advantage by public encouragement of electrical science, but a far greater cause of her advancement has been our gross neglect of our own opportunities. If the war has at last opened our eyes to the terrible dangers of national ca' canny, we may comfort ourselves with the following solid unassailable facts: England is the most favourably situated country in the world for deriving public and private benefit from electrical progress. Our population is more conveniently distributed; our fuel supply is far richer and more accessible. England can, if she chooses, have a supply of electricity laid on practically everywhere like water, cheaper than Germany or any other big country on earth, and with this priceless blessing England cannot only defy competition in a wide range of manufacturing industries, but can bring about a wonderful revival of agriculture and abolish domestic drudgery. Whatever Germany can do we can do twice as well in this field if only our people will drop their pettifogging parochial notions of electrical development and support the establishment of single-minded administration from a broad national standpoint. I doubt if any proposal of economic exclusion would strike Germany's business chiefs with so much dismay as the news that Britain had decided to cease dabbling in electricity, and to make the most of her unequalled natural advantages for its unrestricted application to industry." — *Electrical Industries*, December 5, 1917.

PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, December 6, 1917.

Sir J. J. Thomson, O.M., President, in the Chair.

Papers were read as follows:—

"*The Series of Legendre.*" By Prof. W. H. Young, F.R.S.

"*Discharge of Gases under High Pressures.*" By L. Hartshorn.

It is well known that when gas discharges through an orifice from a vessel in which the pressure is p_0 into one in which it is p_1, the rate of discharge is approximately constant from $p_1 = 0$ upwards to some critical value, but then as p_1 further increases, the discharge falls off, slowly at first, afterwards with greater rapidity. In the present investigation, this phenomenon is examined with greater accuracy than has hitherto been obtained.

The pressure p_0 was constant and nearly equal to the atmospheric pressure. The recipient vessel was partially exhausted, the flow of air being maintained by a powerful air-pump. Variations in the flow were detected by slightly choking the entrance to the discharging vessel, and then observing the changes in the pressure-drop due to the choking.

Nozzles of various shapes were used.

In every case it was found that the flow was constant to at least one part in 10,000 for a considerable range of p_1. The critical value of p_1 at which the flow began to change, varied widely for different nozzles, being about $0{\cdot}2\,p_0$ for the convergent and parallel ones, but as high as $0{\cdot}7\,p_0$ for certain divergent ones. Thus the theoretical value for convergent nozzles, viz., $0{\cdot}527\,p_0$ cannot be accepted as applying even approximately to all nozzles.

"*Internal Ballistics.*" By Lieut.-Col. A. G. Hadcock.

This paper deals with the burning of the explosive in the gun and the expansion of the gas, both before and after the charge has been consumed.

The unit of volume is the gravimetric volume v, but the volume of unburnt powder reduces the space behind projectile available for expansion of gas, and the actual gravimetric volume is v'; thus—

$$v' - a = \frac{v - a}{z},$$

where a is co-volume and z fraction of charge burnt.

On firing the gun the action is threefold.

1. The driving band on projectile is forced into the rifling grooves.

2. In subsequent burning of charge, the gas from any fraction, z, of charge expands with consequent reduction of temperature. The still burning powder gives additional heat. The expansion is thus partly adiabatic and partly isothermal, and proceeds according to the law—

$$p\left(\frac{v - a}{z}\right)^e = k, \text{ a constant.}$$

3. After the charge is consumed the gas expands adiabatically.

The second operation is taken first in order to establish general formulæ.

The value of k depends on the resistance of the projectile to motion. Forcing the driving band into the grooves gives a higher value k' than that for the subsequent motion. Mean pressure behind projectile is given by—

$$p = \frac{k}{(v = a)}\left(z^e + \kappa z_{0e}\right)$$

where z_0 is the fraction of charge burnt during the engraving of the band and—

$$\kappa = \frac{k'}{k} - 1.$$

From these expressions, and knowing the rate of burning of cordite under various pressures, formulæ are developed for finding velocity of projectile, position in gun, and pressure of gas. The magnitude and position of maximum pressure are found by a further development of formulæ.

"*Electrostatic Problem of a Conducting Sphere in a Spherical Cavity.*" By Alexander Russell, D.Sc.

The author gives formulæ by means of which the capacity, the electric force between the spheres, and the maximum electric stress on the dielectric between them, can be readily computed in all cases to any required degree of accuracy.

The solutions of these problems are required when determining the ratio of the measure of the electrostatic to the electromagnetic unit of charge by means of a spherical condenser for the calibration of a spherical condenser of variable capacity, for the calibration of a high-tension voltmeter, and for the determination of the electric strengths of insulating materials.

"*The Zeros of Bessel Functions.*" By Prof. G. N. Watson.

The paper contains a statement and discussion of some general theorems concerning the zeros of Bessel functions; the theorems are true for functions of any order, and, unlike results previously known, are of particular interest in the case of functions of high order. It appears that comparatively general considerations of a non-arithmetical type yield fairly precise information concerning the position and numbers of the zeros of the Bessel functions of the first kind. It is doubtful whether results of this character could be obtained without making use of the method of steepest descents which has been prominent in various recent investigations.

Tables of Bessel functions of order $\pm \frac{1}{3}$ are appended, as these functions notably facilitate the numerical calculation of the zeros of functions of high order.

NOTICES OF BOOKS.

A Text-book of Inorganic Chemistry. By A. F. Holleman, Ph.D., LL.D., F.R.A.Amst. Issued in English in co-operation with Hermon Charles Cooper. Fifth English Edition. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1916. Pp. viii+521. Price 10s. 6d. net.

The last edition of this book contains a good deal of new matter, the sections on atomic weights, colloids, &c., having been re-written, while fresh sections have been added on gaseous equilibrium, association, and intermetallic compounds. The characteristic features of the earlier editions are still conspicuous, and the theoretical parts of the subject are admirably treated. Modern prosesses and methods are given special attention, and the student is kept well abreast of the times, recent work being clearly summarised. The book is perhaps not entirely suitable for the use of beginners, but it would be found excellent for revision purposes, and students who had worked through an ordinary school or first year college course in inorganic chemistry would be certain to find it very valuable for amplifying their knowledge of the subject.

A German-English Dictionary for Chemists. By Austin M. Patterson, Ph.D. New York: John Wiley and Sons, Inc. London: Chapman and Hall, Ltd. 1917.

A knowledge of German is almost indispensable to the chemist at present, owing to the large amount of literature which has been published in that language, and although there is every reason to hope that the disproportion between German and English articles and works will not be much longer maintained, in the meantime it is necessary for use to make the fullest use of what Germany has done in the past. A chemical dictionary has been much wanted, and this book will be found very useful. Both technical and ordinary words are given, and an excellent introduction on the use of the dictionary will provide much help in making out the meaning of unusual or compound words. Special attention is given to the difficulties of organic nomenclature, and with the help of the dictionary and a grammar those who know only a little German ought to be able readily to make out the meaning of any ordinary German article on a chemical subject.

Petroli ed Emanazioni Terrestri. ("Petroleum and Terrestrial Emanations"). By Dr. Icilio Guareschi. Torino: Unione Tipografico-Editrice Torinese. 1917.

This monograph contains a lengthy discussion of the origin of petroleum. The first part treats of the occurrence and constitution of petroleum and rival theories as to its organic origin are very fully analysed and criticised. The author goes right back to the earliest suggestions as to its nature and origin, and traces the gradual evolution of modern theories, giving full references to the works of the various authorities whom he has consulted, often adding biographical notes and short accounts of their work in other branches of science. In the second part of the monograph the composition of gaseous emanations is exhaustively discussed, with special reference to the question of the genesis of petroleum, bitumen, and asphalt. The author has made judicious selections from the vast amount of material at his disposal, and the monograph is a careful compilation of the essentials of the most important theories dealing with the origin of petroleum.

MISCELLANEOUS.

Royal Institution.—The following are the lecture arrangements at the Royal Institution before Easter:—Prof. J. A. Fleming, a course of six experimentally illustrated lectures (adapted to a juvenile auditory) on "Our Useful Servants—Magnetism and Electricity"; Prof. W. M. Flinders Petrie, three lectures on "Palestine and Mesopotamia—Discovery, Past, and Future"; Prof. Arthur Keith, Fullerian Professor of Physiology, three lectures on the problems of British Anthropology"; Dr. Leonard Hill, two lectures on (1) "The Sufling of Children's Health," (2) "The Climatic Adaptation of Black and White Men"; Sir R. T. Glazebrook, two lectures on "The National Physical Laboratory"; Prof. Spenser Wilkinson, two lectures on "Generalship"—(1) A Battle of Napoleon's (Austerlitz), (2) A Campaign of Napoleon's (1806); Sir Napier Shaw, two lectures on "Illusions of the Atmosphere—(1) Revolving Fluid and the Weather Map, (2) The Travelling Vortex and the Cyclonic Depression"; Edmund Gosse, three lectures on "Three French Moralists and their Influence on the War—(1) La Rochefoucauld, (2) La Bruyere, (3) Vauvenargues"; Sir Alexander C. Mackenzie, three lectures on "War Music—Past and Present"; Prof. William J. Pope, two lectures on "The Chemical Action of Light"; Paul H. Loyson, two lectures on "The Ethics of the War"; Prof. Sir J. J. Thomson, six lectures on "Problems in Atomic Structure." The Friday Meetings will commence on January 18, when Prof. Sir James Dewar will deliver a Discourse on "Studies on Liquid Films." Succeeding Discourses will probably be given by Prof. J. Townsend, Prof. A. S. Eddington, Principal E. H. Griffiths, Prof. Arthur G. Green, Prof. E. H. Barton, Prof. Sir J. J. Thomson, and other gentlemen.

MEETINGS FOR THE WEEK.

Thursday, 27th.
Saturday, 29th.
} Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "Our Useful Servants Magnetism and Electricity," by Prof. J. A. Fleming, F.R.S.

THE CHEMICAL NEWS

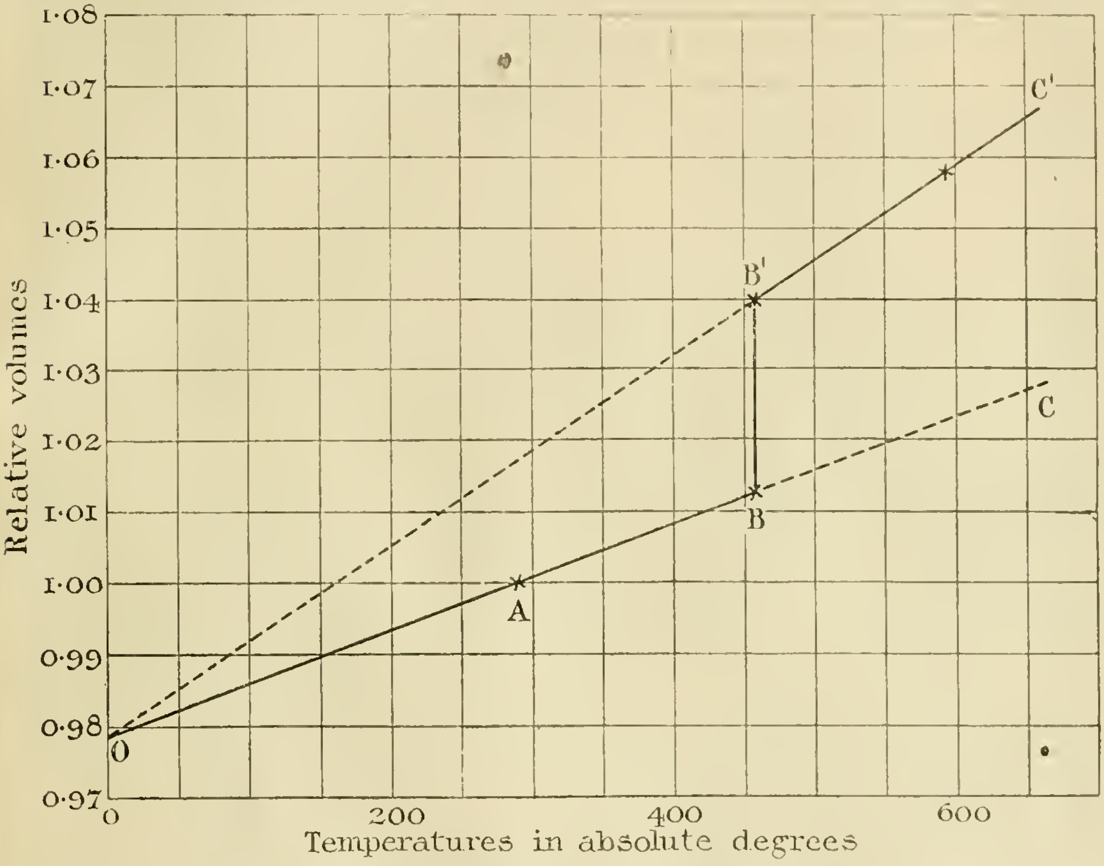
Vol. CXVI. No. 3031.

THE
CONVERGENCE OF THE LIQUID AND SOLID VOLUME CURVES TO ABSOLUTE ZERO

By GERVAISE LE BAS.

When liquids change to solids there is usually an abrupt change in volume on solidification. Three distinct types are recognised :—

(*a*) *Where the Liquid Volume Curve is Steeper than the Solid.*—This results in a more or less abrupt contraction on solidification. Most substances follow this change.



The Relative Volumes of the Tin-lead Alloy.

The Normal Paraffins. C_nH_{2n+1}.

Substance.	d_t	d'.	$\frac{\Delta d}{\Delta t}$	d_{-273}.	V_{-273}	W.	W × 2·34.
$C_{35}H_{72}$	0·7816 (74·7)	0·7664 (99·2)	0·0062	0·9974	493·4	212	496·0
$C_{31}H_{64}$	0·7808 (68·1)	0·7619 (98·8)	0·00616	0·9909	440·0	188	439·9
$C_{27}H_{56}$	0·7796 (59·5)	0·7545 (99)	0·0636	0·9910	383·5	164	383·7

(*b*) *Where the Volume of the Resultant Solid is Greater than that of the Liquid.*—The gradient of the latter is less than in the former case. Ice, &c., are examples of this type of change.

(*c*). In one or two alloys there is a depression at about the melting-point, but examination shows that if the liquid volume curve be produced it will be continuous with the solid curve; that is, they have the same slope.

It is the object of this paper to show that, in general, there is convergence to absolute zero. This is not difficult to understand in the last case, but otherwise it needs demonstration.

An example of case (*a*) is furnished by one of the alloys investigated by Vincentini and Omodei (*Ber.*, xii., 178). The following is a relative volume curve for the whole series:—

The data give the molecular volumes from 17° C. approx. through the melting-point to about 356° C. The volume at 17° is taken as the standard and the volumes at the other temperatures compared with this. It is found that the curves are to a large extent coincident, and the want of coincidence in parts is due to certain disturbances which need elucidation. On producing the curves back ward the liquid curve is found to cut the solid curve at absolute zero (− 273° A.).

Taking the one case mentioned (Sn_3Pb) into consideration it is found

V_{17} (s)	66·81	$V_{182\cdot9}$ (l)	69·44
$V_{182\cdot9}$ (s)	67·65	$V_{275\cdot9}$ (l)	70·24
$\frac{\Delta V}{\Delta t}$	0·005064	$\frac{\Delta V}{\Delta t}$	0·00860
V_{-273}	65·31	V_{-273}	65·52

Δ 0·18 or 0·3 per cent difference.

Phosphorus.

In this case the liquid phosphorus is considered in relation to yellow phosphorus.

Data from Pisati and De Franchis (*Ber.*, viii., 70), boiling-point, 278·3.

	Molten.		Solid yellow.
d_{40}	1·74924	d_0	1·83676
d_{280}	1·52867	d_{44}	1·80681
$\frac{\Delta d}{\Delta t}$	0·00907	$\frac{\Delta d}{\Delta t}$	0·00681
d_{-273}	2·0331	d_{-273}	2·0230
$V(\rho)_{-273}$	15·26	$V(\rho)_{-273}$	15·34

Δ 0·08 or 0·53 per cent.

Red Phosphorus.

d_0 2·15—2·25.

It is thus seen that there is a relation between molten or liquid phosphorus and the yellow solid variety, but not with the red. The latter is much more dense. This shows that the relation of the liquid is with the clear isotropic variety. There is a similar relationship between molten glass and the solid glass, and between water and clear ice. The isotropic character is shown by the geometrical form in which the liquid solidifies, viz., the spherical, a form which is greatly in contrast with the typical geometrical forms of crystals. This is also true of the liquid. This points to the fact that the disposition of the molecules in the liquid and in the solid glass is similar, the only difference being in the relative amount of intermolecular attraction or cohesion.

It may now be shown that the higher paraffins follow the same rule. The data are those due to Krafft (*Ber.*, xv., 1687, 1711; xix., 2218).

In the CHEMICAL NEWS (vol. cxvi., p. 2) it was shown that the volume of hydrogen at absolute zero is equal to 2·340, from a study of solids such as NH_4Cl, $(COOCH_3)_2$, $C_{10}H_8$ [illegible], &c.

It was also shown that extrapolation to absolute zero from the liquid curve gives the same result. It follows that the solid and liquid curves converge to absolute zero. A rather unfortunate error was made in the supposition that no contraction occurs at the melting-point. This is an oversight. There no doubt is a contraction, but this does not invalidate the principle just stated. Krafft does not give data for the solid hydrocarbons so that the evidence is not as complete as in the other cases.

The writer has shown that the metal sodium follows the above rule, also the hydrocarbon naphthalene.

It has long been known that the specific heats of compounds vary in a similar manner to that of volumes. Thus the specific heats of liquids are usually greater than those of the corresponding solids. Person has shown that in the cases he observed there was convergence to about −180°. The atomic heats of liquids and especially those of solids are also well known to be additive. It thus seems necessary to refer the variations of volumes and heat capacity to the individual atoms, and, moreover, to suppose that there is an interdependence of these physical properties. It may thus be possible eventually to compare the energy content of the atoms from absolute zero with the atomic volumes, and possibly to find a law connecting the two. This would lead to an exact understanding of the kinetic conditions ruling in molecules.

THE IDENTIFICATION AND ESTIMATION OF ZINC IN WATER.

PART III.

By ROBERT MELDRUM.

The Ferrocyanide Colorimetric Process.

THE author has undertaken a critical examination of this process for reasons which were stated in a paper contributed to the CHEMICAL NEWS (cxvi., 275). It was then pointed out that estimations made by this process were from 50 to 100 per cent too high when distilled water was used as the standard, and that correct results were only obtained when the standard used had a similar saline content to that of the sample, as the following experiments will demonstrate.

Expt. 1.—100 cc. each distilled and tap water + 0·001 Zn + 1 cc. 20 per cent HCl + 1 cc. 5 per cent $K_4Fe(CN)_6$. In three minutes tap water gave very strong pronounced opalescence; distilled water gave about 70 per cent less opalescence. Tap water with acid and $K_4Fe(CN)_6$ as blank gave no trace of opalescence in fifteen minutes. This equals 1 Zn per 100,000 parts.

Expt. 2.—100 cc. each of distilled and tap water + 0·0004 *Zn* + 1 cc. 20 per cent HCl 1 cc. 5 per cent $K_4Fe(CN)_6$. In five minutes tap water yields pronounced opalescence; distilled water very faint. Repeated this with same result. *Zn* = 1 per 250,000.

Expt. 3.—100 cc. each distilled and tap water + 0·0004 Zn + 0·5 cc. 20 per cent HCl + 1 cc. 5 per cent $K_4Fe(CN)_6$. Tap water, pronounced opalescence; distilled water, faint. Zn = 1 per 250,000.

Expt. 4.—100 cc. each distilled water + 0·0005 *Zn* 1 cc. 5 per cent ferrocyanide with 3 cc., 1 cc., 0·5 cc., 0·25 cc. 20 per cent HCl. All same intensity in opalescence.

The above experiments clearly show that, with variable proportions of acid and zinc contents, distilled water always yields weaker opalescences than tap water, and therefore when used as a standard in water zinc estimations will yield results varying from 50 to 100 per too high. The tap water used had a hardness of 30° and contained 26 parts $CaCO_3$ per 100.000. It was free from Pb, Cu, zinc, and Fe. The experiments also show that zinc can be easily identified even in distilled water at a dilution of 1 in 250,000. It may be mentioned that the zinc was added to the tests in the form of chloride. The HCl used was 20 per cent strong acid by volume in distilled water.

Effect of various Acids.

The question arose as to the use of the most suitable acid and strength of same in continuation of the experiments, and as to sensitiveness.

Expt. 5.—100 cc. each tap water + 0·0003 *Zn* + 1 cc. 1 per cent $K_4Fe(CN)_6$ + 1 cc. each of 10 per cent acetic acid, 10 per cent HNO_3, 10 per cent H_2SO_4, 20 per cent HCl. The percentage is by volume. All the above acids yield opalescences of equal intensity with the *exception* of acetic, which gives none. *Zn* = 1 in 333,000. The opalescence is quite prounounced in each case and does not vary in equality within thirty minutes.

Expt. 6.—50 cc. distilled water 0·0004 *Zn* + 1 cc. 1 per cent $K_4Fe(CN)_6$ with 1 cc. 20 per cent HCl, 20 per cent HNO_3, 20 per cent acetic. In this case acetic acid yields an opalescence, no doubt due to excess of acid, but half the intensity only of that by HCl and HNO_3. The two latter are of equal intensities, the nitric acid giving a greenish tinge to the solution.

Expt. 7.—100 cc. each of tap and distilled water + 0·0005 Zn + 1 cc. 1 per cent $K_4Fe(CN)_6$ + 1 cc. 20 per cent HNO_3. Tap water twice as strong in opalescence. Tap water with ferro. and acid only, but no zinc, in thirty minutes gave no trace of opalescence. This high concentration of acid does not affect the greater intensity of the tap water.

Expt. 8.—100 cc. distilled water; 80 cc. distilled water + 20 cc. CO_2-saturated distilled water. Each with 0·0004 Zn + 1 cc. ferrocyanide + 1 cc. 20 per cent HCl. Both of equal intensity in opalescence. The CO_2 therefore liberated from the hard water on addition of the acid is not the cause of increased opalescency of hard water.

Expt. 9.—100 cc. each of distilled water + 2 cc. 5 per cent $K_4Fe(CN)_6$ + 4 drops of strong acetic acid with 0·01, 0·005, 0·002 Zn. All yield distinct opalescences. Thus with concentration of from 1 in 10,000 to 1 in 50,000 acetic acid yields opalescences; but at greater dilutions the zinc ferrocyanide is apparently soluble.

The above experiments point to the fact that, in comparatively very acid solutions, zinc ferrocyanide is not soluble even at dilutions of 1 Zn in 333,000, or 1 mgrm. in 333 cc. Hydrochloric acid is no doubt the most suitable one to use, as it is the lowest in molecular weight. As will be shown later, even with 1 cc. 20 per cent HCl, 1 part Zn as zinc ferrocyanide in 1,000,000 parts distilled water is insoluble in this acid.

Effect of Ratio of Ferrocyanide.

As 1 part zinc requires for its conversion into zinc ferrocyanide 4·3 parts potassium ferrocyanide, it is important to know the ratio of $K_4Fe(CN)_6$ added to that of the zinc present.

Expt. 10.—100 cc. each of distilled water + 0·0005 Zn + 1 cc. 20 per cent HCl with 1 cc. and 0·25 cc. 5 per cent solution $K_4Fe(CN)_6$. The weaker solution produces twice as much turbidity as the strong one, but is a shade greener. Zn = 1 per 200,000. Ratio ferrocyanide to zinc = 100 and 25 to 1. It would therefore appear that zinc ferrocyanide is soluble in great excess of the potassium salt.

Expt. 11.—100 cc. each tap and distilled water + 0·0005 Zn + 1 cc. 20 per cent HCl + 0·25 cc. 5 per cent $K_4Fe(CN)_6$. Turbidity of tap water twice as strong as distilled. Zn = 1 in 200,000. Ratio of ferrocyanide to zinc = 25 to 1. Even with this low ratio of reagent the difference between tap and distilled water still persists.

Expt. 12.—100 cc. each of distilled water + 0·001 Zn with 2, 4, and 6 cc. 1 per cent solution ferrocyanide. In ten minutes the resulting turbidities are all equal in intensity. The addition of 1 cc. of 20 per cent solution HCl does not weaken turbidity. Zn = 1 in 100,000. Ratio of $K_4Fe(CN)_6$ to zinc = 20, 40 and 60 to 1. This points to the fact that 2 cc. of 1 per cent of the ferrocyanide salt is sufficiently strong for general use in the test, and above this excess to be avoided.

Expt. 13.—100 cc. each of distilled water with 0·0002 Zn, no acid + 1 cc. and 2 cc. 1 per cent ferrocyanide salt. Both of equal intensity in opalescence in fifteen minutes, but very faint. Trace of opalescence by horizontal view, more pronounced vertically. Zn = 1 in 500,000. Ratio ferrocyanide salt to zinc = 100 and 200 to 1. Even with this extreme zinc dilution and so great an excessive amount of reagent the zinc ferrocyanide is not soluble. This is in neutral solution.

Expt. 14.—100 cc. each distilled and tap water + 0·0004 Zn + 2 cc. 1 per cent $K_4Fe(CN)_6$ No acid. Turbidity of tap water three times as strong as distilled in fifteen minutes. Zn = 1 in 250,000. Ratio ferrocyanide to Zn = 50 to 1. The difference between tap and distilled water still persists.

Expt. 15.—100 cc. each tap water + 0·00025 Zn + 1 cc. 20 per cent HCl with 0·25, 0·5, and 1 cc. 1 per cent ferrocyanide, all give pronounced turbidity of equal intensity even viewed horizontally. Zn = 1 in 400,000. Ratio of ferrocyanide salt to zinc = 10, 20, 40 to 1.

Expt. 16.—100 cc. tap water + 0·005 Zn + 1 cc. 20 per cent HCl + 2 cc. 1 per cent $K_4Fe(CN)_6$ white precipitate which remains in suspension, but on violent shaking breaks up to strong milky fluid. Zn = 1 in 20,000. Ratio ferrocyanide to zinc 4 to 1. In this and many other tests it is shown the tendency to form a precipitate of a flocculent nature when insufficient ferro is added.

Expt. 17.—100 cc. each of tap water + 0·005 Zn + 1 cc. 20 per cent HCl with 1, 2, and 4 cc. 1 per cent ferrocyanide.

1 cc. $K_4Fe(CN)_6$,	No turbidity or opalescence.
2 cc. ,, ,,	Pronounced very strong turbidity.
4 cc. ,, ,,	Turbidity not so strong as with 2 cc.

Zinc in solution = 1 in 20,000. Ratio ferrocyanide to zinc = 2, 4, 8, to 1. Here it is seen that insufficient reagent produces no turbidity, and excess produces a weaker turbidity. This experiment points out more than any other the weakness and limitations of the ferrocyanide colorimetric process.

Expt. 18.—100 cc. each distilled water + 0·001 Zn + 1 cc. 20 per cent HCl with 0·5, 1, 1·5, 2, and 3 cc. 1 per cent solution $K_4Fe(CN)_6$.

0·5 cc.	Turbidity strongest of all.
1·0 cc.	Turbidity weaker than above by 10 per cent.
1·5 cc.	Turbidity 50 per cent weaker than with 0·5 cc.
2·0 cc.	Turbidity 20 per cent weaker than with 1 cc.
3·0 cc.	Turbidity 20 per cent weaker than with 1 cc.
6·0 cc.	Turbidity equals No. 2 and 3 cc.

This experiment was repeated several times with the same result, the turbidities in each case remaining constant for twenty minutes. It therefore follows that maximum turbidity is obtained when the ratio of ferrocyanide to zinc is 4·3 or 5 to 1, and that there is a decreasing intensity until the ratio of 20 to 1 is reached. At greater ratios the turbidity remains constant. It is not necessary here to enter into the causes of this phenomena; but it appears not to be due to solubility of the zinc ferrocyanide in that of the potassium salt.

In applying the ferrocyanide method to water testing it is important to note that the ferrocyanide solution must be made up accurately, and accurately measured into the water. Also when the zinc is only present to the extent of about 1 part per million, excess of reagent must be avoided so as to procure as strong an opalescence as possible. The sensitiveness of the reagent, therefore, depends on the exact ratio of reagent to zinc, and points to the importance of fresh ferrocyamide solution being used in the testing. However, the fact remaine that with equal ratios of $K_4Fe(CN)_6$ and zinc equal turbidities result.

Effect of Saline Matter.

The concentration and nature of the saline matter present in water appears to have a modifying influence on the degree of turbidity produced by increasing its intensity, as the following experiments will show.

Expt. 19.—100 cc. each tap and distilled water + 1 cc. 20 per cent HCl + 1 cc. 5 per cent $K_4Fe(CN)_6$ + 0·001 Zn. Tap water 25 per cent more turbid. Added another 1 cc. reagent to each with same result. To distilled added 0·01 grm. NaCl; no increase in turbidity.

Expt. 20.—100 cc. distilled water + 0·0005 Zn = 1 Zn in 200,000 + 1 cc. 20 per cent HCl + 1 cc. 5 per cent $K_4Fe(CN)_6$. Another similar test, but with 0·01 $MgSO_4$ and one with 0·01 $Al_2O_3(SO_3)_6$ all gave equal intensities of opalescence.

Expt. 21.—100 cc. distilled water and tap water + 0·0005 Zn + 1 cc. 20 per cent HCl + 1 cc. 1 per cent ferrocyanide. To the distilled water was added 0·02 grm. $CaCO_3$. The resulting opalescences were equal, whereas with distilled water alone a weaker opalescence resulted. $CaCl_2$, therefore, even at this extreme dilution, increases the intensity of the turbidity.

Expt. 22.—100 cc. distilled water + 0·02 $CaCO_3$ and 0·004 $CaCO_3$ + 0·0005 Zn + 2 cc. 20 per cent HCl + 2 cc.

1 per cent $K_4Fe(CN)_6$. Two blank experiments, but without Zn, were also made. Blanks gave no opalescence in twenty minutes.

0·02 $CaCO_3$ gave pronounced opalescence.
0·004 „ „ weaker „

Zn = 1 in 200,000. Ratio reagent to Zinc = 40 to 1. Therefore as the salinity increases so does the turbidity.

Expt. 23.—100 cc. distilled water + 0·02 cc. $CaCO_3$ + 0·0001 Zn + 2 cc. 20 per cent HCl + 1 cc. 1 per cent $K_4Fe(CN)_6$. In fifteen minutes trace of opalescence when viewed horizontally, and compared with water only, opalescence is distinctly evident. Ratio ferrocyanide to zinc 100 to 1. It is interesting to observe that even when excess of reagent is very great and in the presence of very dilute $CaCl_2$ solutions the zinc is readily detected when present to the extent only of 1 per million.

Expt. 24.—100 cc. distilled water + 0·0005 Zn + 0·02 NaCl gives a turbidity much stronger than with 0·02 $CaCl_2$. With 0·04 NaCl turbidity about 50 per cent less than with the weaker NaCl solution. Ratio ferrocyanide to Zn = 20 to 1. When the ratio is increased to 40 to 1 no difference in intensity was observed.

Expt. 25.—100 cc. each of tap water + 1 cc. 20 per cent HCl + 1 cc. $K_4Fe(CN)_6$ 0·0001 Zn. Distinct trace of opalescence developed. To one tube added 0·01 NaCl; the opalescence becomes nearly twice as great. From this and other experiments there is no doubt that NaCl at concentrations of 100 per 100,000 increase the intensity of the turbidity.

From the above experiments it is clear there is some relationship between the degree of turbidity produced in any given zinc solution, and the kind and concentration of the saline matter present. The system as expressed by concentration of zinc chloride + free ferrocyanide + saline matter must be a very complex one leading to errors under the most favourable conditions when the saline factor is not known. This points to tha fact that the same kind of zinc-free water as the sample must be used as the standard when absolutely accurate results are desired, otherwise when distilled water is used as standard the results are likely to be from 50 to 100 per cent too high.

December 14, 1917.

A CONTRIBUTION TO THE THEORY OF SOLUTION.*

By E. J. HARTUNG, B.Sc.

(Concluded from p. 300).

Aniline and Carbon Tetrachloride.

The experimental results for this liquid pair are given in the following tables:—

Table IX.—*Contractions at 25°.*

M.	N.	D.	V.	Δ_v.
10	0	1·01748	9·1468	0
15·46	0·0996	1·07856	9·1898	0·129
29·60	0·2028	1·14087	92·382	0·232
41·03	0·2962	1·19636	92·843	0·293
51·87	0·3947	1·25364	93·372	0·316
62·08	0·4976	1·31273	93·930	0·330
71·17	0·5990	1·36962	94·527	0·303
79·06	0·6955	1·42275	95·110	0·250
87·05	0·8027	1·48057	95·791	0·167
93·51	0·8971	1·53065	96·403	0·080
98·14	0·9696	1·56853	96·876	0·006
99·39	0·9896	1·57938	96·991	0·005
100	1·0000	1·58469	97·068	0

Table X.—*Heat Capacity at 25°.*

M.	N.	S.	C.	Δ_c.
0	0	0·484	45·02	0
15·46	0·0996	0·446	44·18	0·52
29·96	0·2056	0·409	43·05	0·83
40·47	0·2915	0·377	42·05	1·00
51·87	0·3947	0·349	40·84	1·19
62·08	0·4976	0·321	39·50	1·25
71·17	0·5990	0·295	38·20	1·33
79·99	0·7075	0·268	36·45	1·06
87·05	0·8027	0·244	34·78	0·68
93·85	0·9022	0·223	33·16	0·42
100	1·0000	0·204	31·41	0

Table XI.—*Heat Change at 25° (Negative).*

M.	N.	E.	Δ_E.
14·67	0·0942	98·6	97·4
27·26	0·1848	162·1	169·0
41·52	0·3005	212·7	236·8
53·99	0·4152	238·7	282·3
60·67	0·4827	237·8	291·0
66·93	0·5504	235·1	297·5
73·08	0·6215	220·9	288·9
80·76	0·7175	197·3	269·7
86·07	0·7888	174·6	246·2
91·22	0·8627	129·2	188·0
94·31	0·9092	100·3	148·8

Table XII.—*Contractions at 20°.*

N.	Δ.
0·1	0·45
0·2	0·79
0·3	1·06
0·4	1·27
0·5	1·30
0·6	1·16
0·7	0·97
0·8	0·72
0·9	0·42

The curves drawn from these three sets of results are given in Figs. 11, 12, and 13 respectively. The contraction curve (Fig. 11) shows a relatively small volume change, the maximum effect being in the neighbourhood of N = 0·46; also the curve exhibits a point of inflection towards the carbon tetrachloride end and the gradient possibly becomes equal to 0 at the termination of the curve. The reality at this point of inflection has been carefully verified by repeated experiments. However, the heat capacity deviation curve (Fig. 12) shows no sign of this peculiarity; it also reaches a maximum at N = 0·52. The heat change curve (Fig. 13) is similar in these respects, but is remarkable for the very large heat absorption which it exhibits. This is peculiar when contrasted with the small volume contraction shown, instead of a not unreasonably expected expansion.

Again, the single solvate theory is inadequate to explain the results. It is not quite clear why the contraction curve is the only one showing the point of inflection. If it were due to a solvate containing more than one molecule of aniline in its composition, one might expect the deviation curves of other properties to show some evidence of a similar peculiarity. On the other hand, it may be due to slight association of the carbon tetrachloride, which influences the density of the mixtures to a greater extent than it does the heat capacity and the heat absorption on mixing.

Ether and Chloroform.

This case has been investigated by Dolezalek and Schulze (*Zeit. Phys. Chem.*, 1913, 83), and they claim to have shown that the supposition of the presence of a solvate of equimolecular composition explains the experimental results determined for several properties of mixtures of these liquids. However, their curves show considerable

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* A Paper read before the Faraday Society.

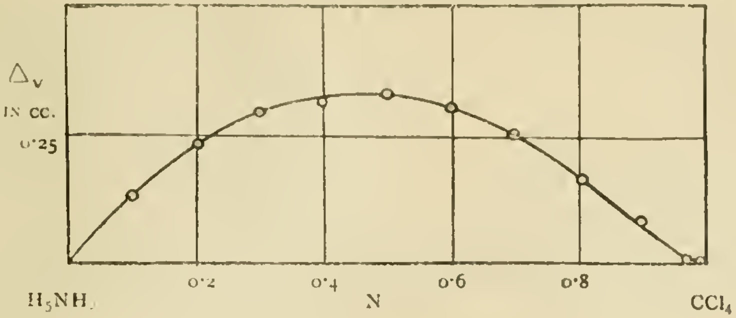

Fig. 11.

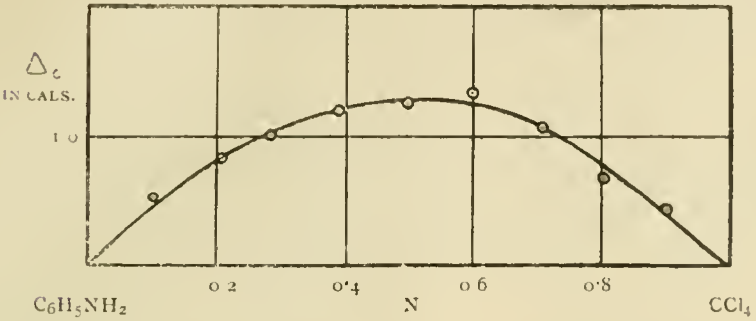

Fig. 12.

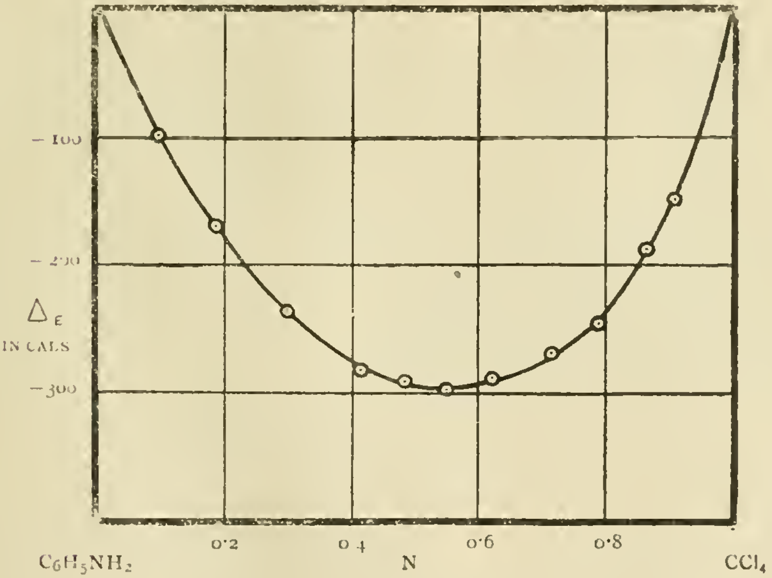

Fig. 13.

deviations from perfect symmetry, which is required by their argument. Their figures for the contractions observed are given in Table XII., their notation having been changed into that adopted in this paper.

N represents the synthetic molar fraction of chloroform in the mixture and Δ the contraction per one total synthetic molecule of the mixture, in cc.

The deviation from symmetry is apparent from a single inspection of these figures; again, if *k* (the property constant) and K (the equilibrium constant) are calculated as indicated in the theoretical part of this paper, different results are obtained according to where the two points on the curve necessary for the calculation are selected. Thus, using as data—

$$N = 0{\cdot}2 \qquad \Delta = 0{\cdot}79$$
$$N = 0{\cdot}5 \qquad \Delta = 1{\cdot}30$$

we get—

$$k = 10{\cdot}2 \quad \text{and} \quad K = 1{\cdot}24\,;$$

but if we use as data—

$$N = 0{\cdot}4 \qquad \Delta = 1{\cdot}27$$
$$N = 0{\cdot}7 \qquad \Delta = 0{\cdot}97$$

we get—

$$k = 3{\cdot}35 \quad \text{and} \quad K = 0{\cdot}02.$$

The value for K obtained by Dolezalek and Schultze from vapour pressure considerations is $K = 2{\cdot}96$.

It is evident that this case also cannot be treated from a single solvate standpoint, and we must postulate the existence of two or more solvates.

The evidence adduced in this paper shows that, in the cases examined, no simple solvate theory will suffice to explain the experimental results, even though the liquids used, with one exception, are little associated. Also, a study of the deviation curves obtained from many other liquid pairs by various authors leads to the conclusion that only in rare cases, if at all, will the conditions be simple enough to permit of an explanation of the deviations by single solvate formation. In the great majority of cases, the molecular condition of a mixture of two liquids is much more complex, and it becomes very difficult to develop and apply any satisfactory quantitative theory.

The author expresses his sincere thanks to Prof. Orme Masson for suggesting the work and for his continual interest and help, especially in the theoretical part, during its performance.

ISO-PIESTIC SOLUTIONS.*

By W. R. BOUSFIELD, K.C., F.R.S.

It was natural that in the development of the broad general outlines of the dissociation theory by Arrhenius and others the smaller discrepancies between theory and experiment should be passed over and their consideration postponed. Now, however, that the source of these discrepancies, in the case of aqueous solutions, has in many cases been traced to the composite character of the solvent water, to the changes which take place in its constitution in the presence of a solute, and to the combinations between solvent and solute which usually occur, the study of these discrepancies promises to be fruitful.

As an example of the generalisations which can only be regarded as first approximations, one may refer to the statement of Nernst that "Iso-osmotic solutions contain the same number of molecules of dissolved substance in a given volume at a given temperature, and the number is the same as in an equal volume of a perfect gas at the same temperature and pressure."

Arrhenius and others speak of two solutions which are in osmotic equilibrium with one another as being iso-osmotic or iso-tonic, and come to the conclusion that solutions containing equivalent or equimolecular quantities per litre are iso-osmotic. Arrhenius further describes solutions which do not change their dissociation on mixing as iso-hydric, and describes iso-hydric solutions as containing the same number of grm.-ions per litre.

So far as the terms iso-tonic, iso-osmotic, and iso-hydric merely express physical facts they may be used with accuracy, but it is now recognised that the propositions involving molecular proportions per litre which they are used to connote as above are only first approximations, and they cease to be even approximate when applied to more concentrated solutions. In various papers I have endeavoured to correlate the various osmotic data with the number h of molecules of water per mol. of solute, and to deduce the number n of molecules of water combined with a mol. of solute. (See a paper of mine contributed to the recent discussion on Osmotic Pressure, *Trans. Faraday Soc.*, xiii., October, 1917, and the former papers to which reference is there made). With the object of deducing these numbers from vapour pressure I began in 1913 a series of measurements of vapour pressures which are still incomplete, but as the completion of the work may be long delayed it seems desirable to indicate the general character of the method and its results in this brief paper.

The method of experiment was determined upon after a number of trials of very various methods and apparatus, to which it is not now necessary to refer. Briefly, the method finally adopted consisted in placing the salts or solutions to be observed in separate open vessels in a common receptacle, which was evacuated to facilitate the exchange of vapour between the solutions in an aqueous atmosphere common to them all, maintained at a uniform temperature. Under such circumstances equilibrium can only be reached by the several solutions gaining or losing water until they arrive at the same vapour pressure. Solutions under such conditions may be said to become iso-piestic. A special word is desirable to denote solutions of equal vapour pressure, since the words iso-tonic, iso-hydric, and iso-osmotic have come to connote theoretical considerations, and are sometimes used inaccurately, whilst the word iso-piestic simply expresses *a fact*, viz., the equality of vapour pressure of the solutions. Iso-piestic solutions must be, of course, strictly iso-osmotic, since it is the equality of vapour pressure which determines osmotic equilibrium.

The purpose of the main investigation was to determine the relative degrees of hydration of iso-piestic solutions of different salts. Thus, for instance, it was found that for solutions of the following salts, after their solutions had stood in the same aqueous atmosphere for several days at a temperature of 18° C. to arrive at final equilibrium, the values of h were—

KCl, $h = 12{\cdot}43$ NaCl, $14{\cdot}23$ LiCl, $17{\cdot}18$

Such solutions are therefore iso-piestic at 18° C.

Some hundreds of experiments were made, covering the range from concentrated to dilute solutions, but owing to certain difficulties of manipulation the general results have not yet been completed. But from the experiments selected valuable deductions can be drawn, which will serve to indicate the capabilities of the method.

Four cylindrical glasses of about 5 cm. diameter and 4 cm. deep were arranged on a tin stand, by means of which they could be easily lifted into and out of a Hempel desiccator. Each glass was furnished with a loose ground cover and a piece of platinum for occasional stirring. The lid of the Hempel desiccator was well ground so as to make a good joint with the body, the joint being luted with vaseline. The lid was also furnished with a well ground tap. The trough of the lid was used to contain a little water or drying substance, as required.

Four pure salts were taken, viz., KCl, NaCl, LiCl, and KNO_3 (in weights of 2 to 3 grms.), dried and placed hot in the glasses, with stirrers and covers previously weighed, cooled in the evacuated desiccator and weighed. The first three had been melted into beads on platinum. The glasses were then arranged on the stand and placed in the desiccator, the covers removed, the desiccator closed, with a little water in the trough, and evacuated by means of a good filter pump, capable of reducing the pressure to about that of the water vapour. The external tube of the tap was then closed by means of a rubber tube and stopper and the desiccator immersed in a large water-bath kept at a regulated temperature of about 18° and constantly stirred. After an interval of one to three days the desiccator was taken out of the bath and opened, the covers replaced on the glasses, and each glass weighed to ascertain the amount of water taken up by the salt. A little more water was now placed in the trough and the process repeated.

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[*] A paper read before the Faraday Society, December 12, 1917.

The result of the earlier stages of an experiment are given in Table I.

TABLE I.—*Successive Values of* h *at* 18° C.

	KCl.	NaCl.	LiCl.	KNO_3.
1913				
Nov. 12	0	0	8·02	0
15	0	0	8·55	0
17	0	0	9·34	0
19	0	0	9·82	0
21	0	0	10·33	0
23	0	0	10·79	0
25	0	0·005	11·24	0
28	0	0·297	11·45	0
Dec. 1	0	1·10	11·59	0
5	0	1·86	11 40	0
7	0	2·09	11·37	0
12	0	5·37	11·34	0
16	0	7·68	11·41	0
20	0	8·21	11·39	0
25	0	8·86	11·42	0
26	0	8·98	11·41	0
28	0	9·08 all dissolved	11·41	0
30	0	9·08	11·40	0

The vapour pressures at each stage can be ascertained from those of the LiCl solutions, which furnish a convenient scale of pressures. It will be observed that up to November 23 the vapour pressure is being continually increased by drops of water added, sometimes in the trough and sometimes to the LiCl solution, but none of the other salts takes up any water from the aqueous vapour in the desiccator.

On November 25 the attack of the water on the NaCl has begun, and after this date it proceeds rapidly, the vapour pressure from November 28 to December 30 remaining practically constant and equal to that of a saturated solution of NaCl. The concentration of the LiCl varies between $h = 11·59$ and 11·37, but this is due to equilibrium conditions not being always established at the time of weighing. On December 28 all the NaCl crystals were dissolved, and we therefore have $h = 9·08$ for a saturated solution of NaCl corresponding to a vapour pressure given by the $h = 11·40$ LiCl solution.

Strictly speaking, the observation of November 25 leaves open the possibility of there being a solid hydrate of NaCl with a lower vapour pressure corresponding to $h = 11·24$ for LiCl. But $\frac{1}{2}$ per cent of water with NaCl corresponds to a hydrate composed of 60 mols. NaCl to 1 mol. of water, and the existence of such a hydrate is unlikely. The existence of a trace of hygroscopic impurity is the more probable explanation.

Another series of experiments gave the critical point at which NaCl begins to take up water as the vapour pressure oorresponding to—

NaCl, $h = 9·18$ LiCl, 11·49

This was in March, 1914, when the thermo-regulator was probably running at a slightly higher temperature than in December, 1913.

Table II. takes up the same series from the point reached on December 28, when the NaCl had just all dissolved and formed a solution saturated at 18°.

It will be observed that the KCl and KNO_3 remained substantially unattacked by water until January 5, 1914, from which point, until February 4, the vapour pressure remains substantially constant at the pressure of saturated KCl, which is probably slightly lower than that which corresponds to the last stage. Here, again, the first attack of the water on the KCl on January 3 is at a pressure slightly lower than the vapour pressure of saturated KCl, possibly owing to traces of a hygroscopic impurity.

Another series which arrived at equilibrium with aturated KCl in April, 1914, gave the following final values:—

KCl, $h = 12·43$ NaCl, 14·22 LiCl, 17·16

TABLE II.—*Successive Values of* h *at* 18° *(continued).*

	KCl.	NaCl.	LiCl.	KNO_3.
1913				
Dec. 30	0	9·08	11·40	0
31	0	10·71	13·05	0
1914				
Jan. 2	0	12·18	14·67	0
3	traces	13·54	16·12	0
5	0·38	14·52	17·17	0
6	3·21	14·41	17·36	0
7	5·20	14·29	17·26	0
8	7·66	14·25	17·20	0
10	9·61	14·17	17·08	0
11	10·02	14·14	16 97	0
12	10·22	13·99	16·82	0
13	10·54	14·07	16·89	0
14	10·90	14·21	16·92	0
16	11·27	14·15	16·98	
17	11·51	14·15	17·07	
18	11·73	14·14	17·05	
20	11·96	14·10	17·00	0
25	12·02	14·06	16·94	0
26	12·16	14·07	16·95	0
28	12·26	14 05	16·92	0
31	12·43	14·11	16·98	0
Feb. 2	12·40	14·11	16·99	0
4	12·39	14·11	16·98	0

Hitherto there has been no attack on the KNO_3. Table III. takes up the same series from the point where the KCl has dissolved in saturated solution on February 4.

TABLE III.—*Successive Values of* h *at* 18° *(continued).*

	KCl.	NaCl.	LiCl.	KNO_3.
1914				
Feb. 4	12·39	14·11	16·98	0
6	12·46	14·18	17·04	0
8	12·47	14·19	17·07	0
10	12·48	14·20	17·08	0
13	12·76	14·47	17·34	0
15	13·36	15·02	17·84	0
17	13·57	15·29	18·19	0
18	14·11	15·86	18·91	0
20	14·75	16·47	19·46	0
21	15·68	17·35	20·37	0
22	16·57	18·20	21·22	0
24	17·18	18·89	22·06	trace

Unfortunately the series came to an end on February 24, owing to the accidental spilling of a drop of solution. The figures of that date may, however, be taken approximately as giving the point at which dry KNO_3 begins to be attacked, for the following reason. The series of figures given in Table IV. were obtained by the reverse process. The weighed salts were first allowed to absorb water and then to come to equilibrium among themselves. The KNO_3 solution was a saturated solution containing undissolved crystals.

TABLE IV.—*Successive Values of* h *at* 18° C.

	KCl.	NaCl.	LiCl.	KNO_3.
1913				
Nov. 4	13·18	16·09	17·46	7·26
5	14·63	17·23	18·87	3·76
7	15·66	18·06	20·13	0·93

These figures do not represent accurate equilibrium figures, as the process of vapour transfer has not come to an end. But they are interesting as showing the reverse process of the drying of the KNO_3 in the presence of the other solutions.

One important result of the whole series is to show that in each case there is a critical hydration pressure below which no attack is made by the water upon a salt.

The vapour pressure of solid salts which crystallise with water of crystallisation has been studied by Andreæ, Frowein, Pareau, and others, and the principles relating thereto have been shortly formulated by van t Hoff. ("Lectures on Theoretical and Physical Chemistry," English ed., part 1, p. 56). The vapour pressures of the three solid hydrates of copper sulphate furnish one of the most familiar examples. These principles do not appear to have been developed or generally recognised in relation to the solution and drying of anhydrous solid salts. For example, one finds the statement that "pure NaCl is very slightly hygroscopic, taking up about ½ per cent of water from moist air."

The deduction to be drawn from the observations above described is that—

> For a pure salt (such as NaCl), without water of crystallisation, there is, at a given temperature, a certain vapour pressure of water, below which the dry salt surrounded by aqueous vapour will not take up water, and will, if it is not dry, become dried. This pressure may be called the critical hydration pressure of the salt at the given temperature.

If the salt forms a series of solid hydrates, like $CuSO_4$, the critical hydration pressure would be the vapour pressure of the first solid hydrate. If the salt forms no solid hydrates under the given conditions the critical hydration pressure is the vapour pressure of the saturated solution of the salt. The vapour pressure of the saturated solution is, of course, the equilibrium vapour pressure reached when part of the salt is dry and part in solution.

From the known fact that $CuSO_4H_2O$ has a definite vapour pressure of 4·4 mm. (at 50°), and that the vapour pressure is zero for dry $CuSO_4$, one might infer the critical hydration pressure of 4·4 mm. It is well, however, to place the principle on a broader foundation and to formulate it definitely, as it has an obvious practical application in reference to the drying of salts and the consolidation of the crystals into a compact mass under atmospheric influences.

In order to translate the figures above obtained into vapour pressure expressed in mm. of mercury, we require a scale of vapour pressures. If this can be established for one of the salts it gives the vapour pressure for the iso-piestic solutions. A means of doing this is given by the osmotic and ionisation relations established in a former paper (Bousfield, *Trans. Chem. Soc.*, 1809, cv.). It was there shown (*loc. cit.*, p., 1820) that the relation—

$$n = 38a - 14$$

held approximately for the relation between the ionisation a and the number n of combined water molecules in the case of LiCl solutions at 18°. A closer working out of the figures gives the relation as—

$$n = 36{\cdot}3a - 13{\cdot}22.$$

It was also shown that the dilution law—

$$\frac{\alpha^2}{1-\alpha} = K(h-n).$$

was an accurate law, where K could with considerable accuracy be taken as a constant, although the mass action law theoretically demanded a small amount of variability of K with the variation of the composition of the free water of the solution. Neglecting this small variation, we can, from the expressions—

$$n = h - \frac{a^4}{K^2(1-a)^2},$$

$$n = 36\ 3\alpha \cdot 13{\cdot}22,$$

by taking various values for α, make a table of corresponding values of h and n, from which the scale of vapour pressures of LiCl solutions at 18° may be obtained by means of the relation (Landolt Bernstein Tables)—

$$\frac{\delta p}{p} = \frac{1+a}{h-n},$$

where p is the vapour pressure of water at 18° and δp is the vapour pressure lowering.

TABLE V.—*Values of δp/p for LiCl Solutions at 18°.*

a	n.	h.	$\delta p/p$	Difference for $\delta h = 1$
0·44	2·75	7·00	0·3388	
0·45	3·12	7·95	0·3002	0·0406
0·46	3·48	8·95	0·2669	0·0333
0·47	3·84	10·02	0·2379	0·0271
0·48	4·20	11·19	0·2117	0·0224
0·49	4·57	12·46	0·1888	0·0180
0·50	4·93	13·83	0·1685	0·0148
0·51	5·29	15·32	0·1505	0·0121
0·52	5·66	16·95	0·1346	0·00975
0·53	6·02	18·74	0·1203	0·00799
0·54	6·38	20·68	0·1077	0·00649
0·55	6·75	22·83	0·09639	0·00526
0·56	7·11	25·19	0·08628	0·00428
0·57	7·47	27·79	0·07726	0·00347
0·58	7·83	30·67	0·06918	0·00281
0·59	8·20	33·86	0·06196	0·00226
0·60	8·56	37·39	0·05550	0·00183

The validity of this table rests on Tammann's experimental values (Landolt Bernstein Tables) for dp for LiCl solutions of four strengths at temperatures between 40° and 100°. From these the figures at 18° are diagrammatically extrapolated (*loc. cit.*, p. 1812). These extrapolated values are given in Table VI., together with the values calculated directly from Table V. It will be seen that Table V. gives values completely in accord with Tammann's experimental results. The difficulty of obtaining accurate vapour pressures at the low temperature of 18° by direct measurement is very great. Tammann's pressures at higher temperatures, which give a range of 25 values between 40° and 100° for each concentration, furnish a basis for extrapolation which probably leads to more accurate results for 18° than could be obtained by direct measurement. The more accurate and authoritative determination of such a scale for LiCl, by the collaboration of various observers, is greatly to be desired. It would render the determination of the vapour pressure of any solution by comparison with the LiCl standard by the method above described a simple matter.

TABLE VI.—LiCl *Solutions at* 18°.

h	$\delta p/p$ from Tammann.	$\delta p/p$ from Table V	Difference.
7·275	0·326	0·327	1
10·40	0·229	0·229	±
16·25	0·140	0·141	1
29·19	0·073	0·073	±

With the help of Table V. it is now possible to express the critical hydration pressures for KCl and NaCl at 18° in terms of mm. of mercury with some accuracy. The values of h for LiCl solutions corresponding to the critical pressures for the other salts are for LiCl—

KCl, h = 14·50 NaCl, 10·80 KnO_3, 22·00

the value for KNO_3 being only an approximate figure. The values of $\delta p/p$ calculated from Table V. are—

KCl, $\delta p/p$ = 0 160 NaCl, 0·220 KNO_3, 0·101

and the corresponding critical pressures at 18° in mm. of mercury are therefore—

12·92 12·00 13·83

the vapour pressure of water at 18° being taken as 15·38.

We may give a further example of the kind of information which iso-piestic solutions will give us when the basic data for a standard substance are accurately determined. To follow the *modus operandi* in detail it is necessary for the reader to have before him the former paper ("Ionisation and the Law of Mass Action," Part III., *Trans. Chem. Soc.*, 1914, cvi., 1811).

Our two sets of values for solutions iso-piestic with a saturated solution of KCl at 18° are—

KCl.	NaCl.	LiCl.
12·43	14·22	17·16
12·39	14·11	16·98

The mean values are—

12·41	14·16	17·07

From the standard table for LiCl values we get the value of $\delta p/p$ when $h = 17{\cdot}07$ as—

$$\delta p/p = 0{\cdot}1336.$$

For the values of the constant K we have—

KCl, $1/K = 5{\cdot}370$ NaCl, $5{\cdot}821$ LiCl, $5{\cdot}996$

whence we get—

$$\log \frac{K^2}{\delta p/p} \quad \bar{1}{\cdot}41425 \qquad \bar{1}{\cdot}34459 \qquad \bar{1}{\cdot}32283$$

Thence for the values of a we get from the table (*loc. cit.*, p. 1828)—

$$a = 0{\cdot}5395 \qquad 0{\cdot}5251 \qquad 0{\cdot}5207$$

It would thus appear that the ionisation of a saturated KCl solution is greater than that of the iso-piestic solutions of NaCl and LiCl, which is probably connected with the fact that there is more free water in a saturated solution of KCl than there is in the more dilute solutions of the other salts. Since—

$$(h-n)\delta p/p = 1+a$$

we can calculate the free water $h-n$, and we obtain—

KCl, $h-n = 11{\cdot}52$ NaCl, $11{\cdot}41$ LiCl, $11{\cdot}38$

from which we get the combined water—

$$n = 0{\cdot}89 \qquad 2{\cdot}75 \qquad 5{\cdot}69$$

for these iso-piestic solutions.

It thus appears that for these iso-piestic solutions the amounts of free water are nearly the same, the balance of the water being made up by the differing amounts of combined water, which are roughly one, three, and six molecules respectively for the different salts, when the free water for all is about eleven and a half molecules.

It is of interest to compare the results for saturated solutions of the three salts at 18°, which are given in Table VII., those for LiCl being taken from the former paper (*loc. cit.*, p. 1823), and those for NaCl being calculated from the iso-piestic data in the mode above described for KCl.

TABLE VII.—*Comparative Data for Saturated Solutions at* 18° C.

	h.	*δp/p.*	*a.*	*h—n.*	*n.*
KCl ..	12·43	0·1336	0·540	11·54	0·89
NaCl..	9·13	0·2072	0·486	7·18	1·95
LiCl ..	3·00	0·875	0·400	1·60	1·40

The above examples will serve to illustrate the kind of results which may be obtained by the study of iso-piestic solutions. The method appears to admit of a *relative* accuracy in the determination of vapour pressures of a high order. The accurate determination of the absolute values of vapour pressures of one substance, such as LiCl, would enable the absolute values of other substances to be readily determined with equal accuracy by the iso-piestic method.

Geologic Time and the Elements.—The paper on the above in your recent issue is interesting, that with satisfactorily determined geological time, and errors in the determination of the atomic weights eliminated, the properties natural to an element in any transformation may be sufficiently defined to establish them.—J. C. THOMLINSON, B.Sc.

NOTE ON THE SYSTEM OF RECORDING RATE OF CHEMICAL REACTION.

By JAMES W. McBAIN, M.A., Ph.D.

THE present method of recording rate of reaction suffers somewhat from lack of directness. Even the chemist familiar with this subject has to pause when he is told that the velocity constant of a reaction is 147×10^{-4}, before he is able to visualise the significance of that information. For this reason the author ventures to make the suggestion that this mathematical value should be replaced by a number which has such direct physical significance that it conveys a mental impression even to those who have not specially familiarised themselves with this subject.

All equations representing rate of reaction may be written in the form—

$$k = \frac{1}{t}\,\text{(remainder of the expression)}.$$

where k is the present rate constant of the reaction and is the time the reaction has been going on.

The equation may be written—

$$kt = \text{(remainder of the expression)},$$

where k and t appear only as a simple product varying in inverse proportionality to each other from case to case. It is necessary, then, to give, not only the value of k, but also the value of the unit of time. Thus k has to be taken sixty times smaller if hours are used instead of minutes.

The proposal outlined in this note is to set k always equal to unity, and to choose the unit of time accordingly. The equation then simplifies to—

$$t = \text{(remainder of expression)},$$

where k disappears altogether.

The first difference is that we give up using whole minutes (or seconds, or hours) as the unit of time, and take instead the new time unit necessary to express the rate in this form. The advantage of this is that a single number such as "3·36 hours" completely records the rate of reaction; whereas the corresponding constant as usually expressed, "$k = 0{\cdot}298$," has to be supplemented by the information that "time is expressed in hours."

The second and important advantage is that the proposed "unit of time" gives a direct idea of the rate of the reaction. Thus, to quote once more the reaction alluded to in the first paragraph, instead of saying that the inversion of menthone in the presence of N/100 HCl at 20° "has a velocity constant equal to 147×10^{-4} and that the time is expressed in minutes," the proposal is merely to state that "the unit of time for this reaction is sixty-eight minutes" (which is, of course, $1/147 \times 10^{-4}$).

The present rate constant k can be given physical significance by recollecting that if the concentrations of all the reacting substances could be kept up to unity (1 grm.-mol. per litre) for unit time—perhaps by adding supplies as required—the number of grm.-mols. of substance reacting would be equal to k.

It appears to me that this is not merely so direct as the statement that "the time unit is sixty-eight minutes," which means that if the concentration were kept up to unity it would take sixty-eight minutes for one grm.-mol. of the substance to react.

The arithmetic involved in both cases is the same. The conversion of values hitherto recorded to the new system merely requires that the reciprocal of k be taken and the word "hours" or "days" or "seconds" or "minutes" added. A third incidental advantage of the system now suggested is the avoidance of small decimals. This arises, of course, from the fact that very few rate constants have been recorded for reactions that are all over in less than a minute, and clearly such reactions do not lend themselves to measurement. Consequently nearly all rate constants are small decimals.

In the case of monomolecular reactions the new "unit of time" gives the time required for the reaction to go to the extent of 63·2 per cent. Further, if multiplied by the natural logarithm of 2 (which is 0·693) it gives the time required for the reaction to go half-way.

Owing to military duty the author has not the opportunity of searching the literature in order to ascertain whether the suggestion contained in this note has already been put forward, but he has no recollection of any previous proposal to do away with the rate constant altogether as a method of recording rate of reaction.—*Transactions of the Faraday Society*.

THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS.*

PART II.—LIQUIDS.

By IRVING LANGMUIR

(Continued from p. 304).

Discussion of Results.

THESE experimental results afford the strongest kind of confirmation of the theory that the spreading of films on surfaces is determined by the shapes of molecules and the relative activities of the different portions of the molecules. The maximum areas given in Table I. are in substantial agreement with the values of a_0 taken from the curves in Figs. 8 to 18. The sharpness with which the force increases as the area available for the film is decreased is an excellent proof of the small range of the forces acting between the group molecules.

The saturated fatty acids (from palmitic to cerotic) cover approximately equal areas per molecule ($a_0 = 21 \times 10^{-16}$ sq. cm.), irrespective of the length of the hydrocarbon chain. The glycerides cover about the same area as the fatty acids obtainable from them. The results with cetyl palmitate, amyl stearate, and ethyl palmitate show that the relations are not always as simple as this and that the areas, even in the case of saturated hydrocarbon derivatives, are not always determined solely by the number of —COO— or other active groups present.

In the case of esters, such as amyl stearate, in which the molecules have two hydrocarbon chains of very unequal length, it is probable that a part at least of the hydrocarbon chain lies in the surface in contact with the water. We shall see, in another part of this paper, that with very dilute solutions of the lower members of the fatty acid series, the molecules lie spread out flat on the surface. Evidently this tendency exists to some extent among certain esters of the higher fatty acids, especially at high temperatures. We will pospone the further discussion of this subject until we have considered the results obtained in connection with the adsorption of fatty acids in the surface of their solutions in water.

The unsaturated fatty acids all cover much greater areas per molecule than the saturated. The double bond in oleic acid is thus apparently drawn down on to the water surface. It is interesting to note, however, that linoleic acid, with its two double bonds, does not cover any greater area per molecule than oleic acid. It may be that the double bonds attract one another to some extent in place of the water. Linolenic acid, however, with three double bonds covers a considerably greater area than oleic or linoleic. As the number of double bonds increases the energy consumed in compressing the film decreases (see Fig. 16), probably because the —COO— groups tend to be attracted by the double bonds in adjacent molecules, and are thus more easily separated from the water surface.

The molecule of ricinoleic acid appears to lie almost wholly flat on the surface, the value of a_0 being in the neighbourhood of 110×10^{-16} sq. cm. In this molecule there are three active groups—carboxyl, hydroxyl, and the double bond. These three together should not cover more than $60-70 \times 10^{-16}$ sq. cm. The value $a_0 = 110 \times 10^{-16}$, corresponds to a film thickness $\tau = 4 \cdot 7 \times 10^{-8}$ cm., which is about what we should expect for a hydrocarbon molecule spread out flat on the surface. The caster oil (triricinolein) molecule is also evidently spread out flat on the surface.

The presence of the sharp kinks in the curves, such as H and V, makes it evident that several different processes are often involved in the compression of a film, and that these occur one at a time. Thus, in compressing a palmitic acid film (Fig. 8) between Q and H the molecules are being squeezed together more and more tightly, but without involving any radical change in their relative positions. When the point H is reached the film begins to crumple up, probably by the folding of the whole film, but possibly by tearing molecules one by one from the surface of the water and squeezing them into a second layer on top of the first.

The kinks in Fig. 9 and in Curve I. of Fig. 12, are undoubtedly due to the solidification of the film.

With films which are liquid, as, for example, cetyl alcohol films, the kink H probably occurs when the active group is forced away from the water surface and a second layer of molecules begins to form.

In attempting to account for the remarkable curves obtained with films of fatty acids on acidulated water it is important to bear in mind that the curves (Fig. 8) obtained on pure water represent wholly irreversible conditions. Even with a liquid film (Fig. 13) the Curve UVK obtained by expanding the film, does not even approximate that obtained during compression (QHU). This is probably to be explained as follows:—At the point Q all the molecules of cetyl alcohol lie on the surface with the OH group in contact with the water and the hydrocarbon chains vertical. As the force of compression is increased the molecules are subjected to forces quite analogous to those acting on a watermelon seed squeezed between the fingers. In this latter case a very considerable pressure may be exerted before the seed moves at all; when it does, however, it is projected with high velocity. Similarly, the molecule of cetyl alcohol may be acted on by strong forces without causing it to be pulled away from the water surface. When the force reaches a certain value, however, the molecule is ejected. The energy involved may be much greater than that theoretically required to separate an OH group from the water surface. This ejection of molecules first begins when the point H is reached.

Now after a molecule has been forced into the second layer, its active group cannot come in contact with the water at all. If the force on the film is decreased (as at U in Fig. 13), the film therefore does not at first tend to spread. If the force is sufficiently decreased (for instance, to V), then the thermal agitation causes some gaps in the first layer to form from time to time, and into these the molecules in the second layer may descend until they come in contact with the water. This causes a spreading of the film.

The presence of hydrochloric acid in the water seems to cause an increase in the effective volume of the —COOH group, probably by adsorption of hydrogen ions. When the film is compressed the hydrocarbon chains are thus held so far apart at their lower ends that they cannot pack together in the manner necessary to form a solid film. As the force is increased the adsorbed ions (?) on the —COOH groups are forced off until (at L, Fig. 11) the —COOH groups may occupy the same area as if no acid were present. The film, for some unknown reason, remains liquid (except Curve I., Fig. 12), and the molecules are thus more easily ejected (at H) into the second layer. The hydrogen ions thus act as a catalyser in two ways—by increasing the mobility of the film and by making it easier for the molecules to pass into the second layer. This is not caused, however, by any decreased attraction between the water and the —COOH group. (This conclusion is based on the fact, discussed in a forthcoming paper by Harkins, that the surface tension at the interface of oils is not appreciably affected by the presence of acid)

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* From the *Journal of the American Chemical Society*, xxxix., No. 9.

The action of hydrochloric acid on these films is undoubtedly intimately related to the action of acids in catalysing esterification. It must also be connected with the potential changes observed by Haber and Klemenciewicz and others. (*Z. Physik. Chem.*, 1909, lxvii., 385).

The Structure of Adsorbed Films on the Surface of Liquids.

(A brief preliminary account of part of the work described in this section has appeared in the *Proc. Nat. Acad. Sci.*, 1917, iii., 25).

The films of oil or solid fats described in the preceding section differ from other adsorbed films only by their insolubility and non-volatility. When a soluble fatty acid or alcohol is dissolved in water, or when the vapour of a substance like hexane or benzene is brought into contact with water, the surface tension is very materially decreased. According to the principle enunciated by Gibbs, this indicates that the dissolved substance or the vapour is adsorbed in the surface.

From the viewpoint developed in this paper we should expect that these adsorbed films in general should consist of not more than a single layer of molecules.

By means of Gibbs' equation,

$$q = -\frac{c}{RT}\frac{d\gamma}{dc} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

the amount of material q adsorbed per sq. cm. of surface may be calculated from the rate at which the surface tension γ varies as the concentration of the dissolved substance changes. The equation may also be applied to the depression of surface tension caused by a gas or vapour above the liquid.

(Note.—A simple derivation of this equation is given by Milner—*Phil. Mag.*, 1907, xiii., 96. In this derivation it is not assumed that the gas law $pv = RT$ holds in the surface layer; it is only necessary that it should hold for the osmotic pressure inside the solution, or in the case of adsorbed vapours, for the vapour above the liquid. The equation thus rests on a firm foundation, at least in the case of dilute solutions).

It was pointed out by Milner that when substances which strongly depress the surface tension are added to water the surface tension is a linear function of the logarithm of the concentration of the dissolved substance for all except very dilute solutions. We may write Equation 1 as follows:—

$$q = -\frac{1}{RT}\frac{d\gamma}{d\ln c} \quad . \quad . \quad . \quad . \quad . \quad (2).$$

If γ is a linear function of $\ln c$ then q will be independent of the concentration. Milner thus calculates from Whatmough's data for acetic acid solutions that q is $3{\cdot}8 \times 10^{-10}$ mols. per. sq. cm. over a rather wide range of concentration. The constancy of q under these conditions is readily explained according to our theory as being determined by the number of molecules needed to form a single layer. If we multiply Milner's result for q by N we find that the amount adsorbed corresponds to 23×10^{13} molecules per sq. cm. The area occupied by each molecule is thus 43×10^{-16} sq. cm. This result is in fair agreement with the value 22×10^{-16}, which we have found for films of the higher fatty acids on water. It is probable that each molecule of a substance as soluble as acetic acid is surrounded by water molecules, so that these and the acetic acid molecules are packed in the surface layer alternately, each acetic acid molecule being surrounded by a definite number of water molecules. The CH_3 groups in the acetic acid molecule undoubtedly come to the surface but cover only a part of the surface.

Szyszkowski (*Z. Physik. Chem.*, 1908, lxiv., 385) measured the surface tensions of aqueous solutions of propionic, butyric, valeric, and caproic acids (in each case both the normal and the iso compound) and found that results could be accurately expressed by the empirical relation.

$$\frac{\gamma}{\gamma_0} = 1 - B\log_{10}\left(\frac{c}{A} + 1\right). \quad . \quad . \quad (3).$$

Here γ is the surface tension of the solution, while γ_0 is that of pure water, c is the concentration of the fatty acid in mols. per litre. A and B are constants.

Szyszkowski found that the constant B was the same for all the fatty acids studied, its numerical value being 0·411. A was a constant for any one substance, but its value decreased rapidly as the length of the hydrocarbon chain increased as follows:—

Table II.

	A. Mols. per litre.	Ratio
Propionic acid	0·165	
Butyric acid..	0·051	3·25
Valeric acid..	0·0150	3·40
Caproic acid	0·0043	3·48

(To be continued).

PROPOSED IMPERIAL BANK OF INDUSTRY.

An important report has been issued by the Committee on Banking of the British Empire Producers' Organisation recommending a scheme the main features of which are set forth below.

The general motive of the scheme is to afford readier financial support on sound principles throughout the United Kingdom and the Overseas Dominions and Colonies for producers and manufacturers, and amongst other results it is intended that there shall thus be in any event no opening for German financial intrigue in obtaining control of any group of industry. It is claimed for the scheme that on the one hand it involves no departure from methods which have been successfully demonstrated on a national scale, and on the other hand it conflicts in no way with the ordinary business of joint stock banks, but is, on the contrary, calculated to increase their turnover.

The available capital is to be provided in the shape of debentures and deposits with State guarantee. Further capital will also be accumulated by the funding of profits, as apart from a small bonus to debenture holders and depositors all surplus will remain in the bank.

Guarantee Capital Fifty Millions Sterling.
(To be enlarged as demand shall arise).

Guarantors—

The United Kingdom	£25,000,000
The Dominion of Canada	6,000,000
The Commonwealth of Australia ..	6,000,000
The Dominion of New Zealand ..	2,000,000
The Union of South Africa	2,000,000
Newfoundland	1,000,000
Straits Settlements and Malaya ..	8,000,000
Ceylon	
British Guiana	
Mauritius	
West Indies..	
Rhodesia	
Falkland Islands	
Fiji and other British Possessions ..	
Total..	£50,000,000

Note.—The above figures are suggested only.

Provision is made for government by boards of trustees, on which both employers and employed would be represented.

Objects.

To strengthen and to extend producing and manufacturing industries already established in the Empire.

To assist in the foundation and development of new industries therein.

To assist by credit facilities in the sale of their products.

To assist them in procuring materials, machinery, and facilities from other parts of the Empire.

To assist in the acquisition within the Empire by its citizens of control and utilisation of its own products.

The foregoing to apply only to companies, firms, and individuals of British origin and whose registration is within the British Empire.

Methods.

To carry out the objects by :—

Making advances by way of cash credits against such security or guarantee as the trustees shall deem sufficient.

Accepting drafts made against shipments or deliveries of industrial products or of materials.

Buying and selling bills of exchange against collateral security.

Issuing letters of credit.

Discounting trade bills.

Purchase of secured time payment accounts or by advances upon the same.

To assist and to co-operate with other financial institutions in underwriting the share and debenture issues of present or future industrial undertakings.

To collect and collate information likely to be useful to its customers.

CORRESPONDENCE.

RAMSAY MEMORIAL FUND.

To the Editor of the Chemical News.

Sir,—We are asking the hospitality of your columns to enable us to report the progress of the Ramsay Memorial Fund which was instituted just a year ago with the object of raising a sum of £100,000 as a suitable Memorial to the late Prof. Sir William Ramsay. The fund has now reached a sum of over £30,000. The latest and most important donation to the fund has been a sum of £5000 contributed by Mrs. Wharrie. It may be remembered that Messrs. Brunner, Mond, and Co. have promised a similar sum of £5000. The Honorary Treasurers have received a large number of other sums ranging from £1000 to one guinea. From this it will be seen that the Ramsay Memorial Fund has now passed its experimental stage and is making good progress towards the sum which the Committee aim at raising. The Executive Committee are confident that with the assistance of the large number of co-operating Committees which have been formed they will be successful in completing the fund of £100,000, but in order that this may be the case they must appeal to the generosity of the public for further donations, large and small. They hope that the generous example of Mrs. Wharrie and of Messrs. Brunner, Mond, and Co. will be followed by others, but they will also greatly welcome gifts of any amount ranging from one guinea upwards.

The fund of £100,000, when raised, will be devoted to two objects of great national importance, the establishment of Ramsay Memorial Fellowships for research in chemical problems as applied to industry, and the foundation of a Memorial Laboratory of Engineering Chemistry. Those who contribute to the Ramsay Memorial Fund are contributing in the most definite and direct way to the national prosperity after the war in which the advancement of science must play an increasingly important part. Donations should be sent to the Honorary Treasurers, Ramsay Memorial Fund, University College, Gower Street, London, W.C.—We are, &c.,

Rayleigh, Chairman of the General Committee.
Hugh Bell, Chairman of the Executive Committee.
Glenconner, } Honorary Treasurers.
J. N. Collie, }

MISCELLANEOUS.

Acetic Acid.—With regard to the Order of the Minister of Munitions, dated October 1, 1917, including acetic acid in the war materials to which Defence of the Realm Regulation 30A applies,—Notice is hereby given that, as from the present date, all applications for permits to deal in acetic acid and other applications and inquiries regarding the above mentioned Order should be addressed to the Director of Propellent Supplies, Explosives Supply Department, 32, Old Queen Street, Westminster, S.W. 1. This Notice cancels the footnote to the said Order directing applications and inquiries regarding such Order to be addressed to the Chemical Section, Trench Warfare Supply Department.

Faraday Society.—A General Discussion on "The Setting of Cements and Plasters" will be held on Monday, January 14, 1918, at 5.30 and 8.30 in the Rooms of the Royal Society of Arts, John Street, Adelphi, London, W.C. 2. Dr. C. H. Desch (Glasgow) will open the Discussion with a paper on "The Mechanism of the Setting Process in Plaster and Cement." Prof. H. Le Chatelier will send in a communication on "Crystalloids *v.* Colloids in the Theory of Cements." Mr. A. A. Klein (Worcester, U.S.A.) will send in a paper on "The Constitution and Hydration of Portland Cement." Mr. George A. Rankin (Creighton, U.S.A.) will send in a paper on "The Setting and Hardening of Portland Cement." Mr. Bertram Blount will read a paper on "The Setting of Cement in its Relation to Engineering Structures." Mr. John Rhodin will read a paper on "Note on the Colloidal Theory of Setting." Mr. E. H. Lewis and Monsieur E. Deny (Wisbaw) will read a paper on "The Effect of the Addition of Suitable Slag on the Setting Properties of Portland Cement." Mr. W. J. Dibdin will read a paper on "Ancient and Modern Mortars." Mons. R. Feret (Boulogne-sur-Mer), Mr. A. Binns, Dr. E. B. Butler, Mr. W. J. Cooper (Penarth), Mr. Alex. L. Field (Pittsburgh, U.S.A.), Dr. T. Martin Lowry, F.R.S., and Dr. J. W. Mellor will also contribute to the Discussion.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Decomposition and Solution of Minerals.—I should be obliged if anyone could inform me of a method, or refer me to a book describing a method, of breaking down difficultly soluble minerals. After finely pulverising and sieving a hard mineral there was tried fusion mixture with and without silica, caustic soda, pyrosulphate of soda, and mineral acids, including hydrofluoric acid. None of these were effective. The residue from the fusion mixture was successively treated with pyrosulphate, hydrofluoric acid, and again with fusion mixture. About 25 per cent of a pale bluish residue remained. The soluble matter was chiefly silica, iron, and alumina.—Perplexed.

MEETINGS FOR THE WEEK.

Tuesday, Jan. 1st. } Royal Institution, 3. (Christmas Lectures, adapted to a juvenile auditory). "Our Useful Servants Magnetism and Electricity," by Prof. J. A. Fleming, F.R.S.
Thursday, ,, 3rd. }

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END OF VOLUME CXVI.

LONDON:

PRINTED BY EDWIN JOHN DAVEY,

16, NEWCASTLE STREET, FARRINGDON STREET,

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